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COAL LIQUEFACTION USING ZINC CHLORIDE CATALYST  
IN AN EXTRACTING SOLVENT MEDIUM

Shamim Ahmed Gandhi and Alexis T. Bell  
(M.S. thesis)

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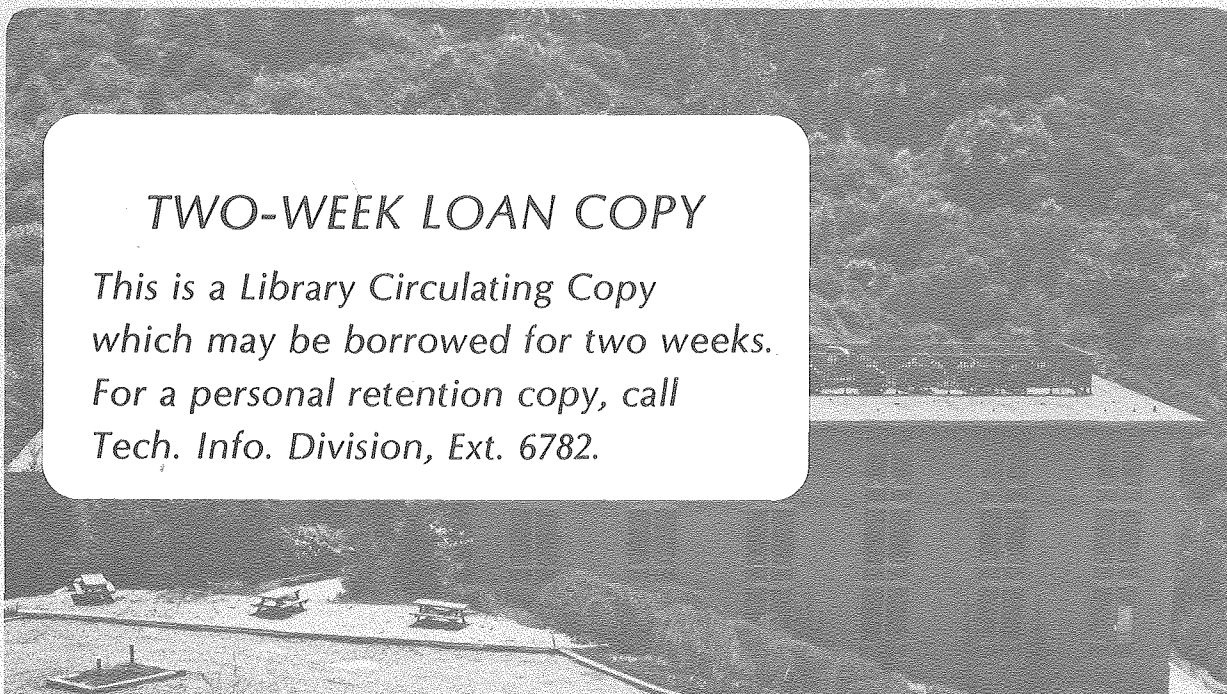
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COAL LIQUEFACTION USING ZINC CHLORIDE  
CATALYST IN AN EXTRACTING SOLVENT MEDIUM

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ABSTRACT

Coal liquefaction was studied in a stirred autoclave using zinc chloride catalyst in a cyclohexane solvent medium. Three different coals were investigated: SRC-I, Wyodak sub-bituminous coal, and Illinois #6 bituminous coal.

At 300°C, 2000 psig, and catalyst to coal weight ratio of 1.0, the presence of zinc chloride increased the cyclohexane solubility of SRC-I from 10.6% to 30.0%, Wyodak coal from 6.9% to 13.5%, and Illinois #6 coal from 1.8% to 8.0%. Data on catalyst loading showed that a catalyst to coal weight ratio of 0.6 was optimum for Wyodak coal and 1.0 for Illinois #6 coal. Studies on the effect of reaction time indicated that the solubility of Wyodak coal increased linearly up to 2 hours, while the solubility of SRC-I was nearly constant after 1 hour. Increasing reaction temperature from 250°C to 400°C was found to linearly increase the yield of soluble products. Hydrogen pressure had a lesser effect on the yield, but the presence of gaseous hydrogen was necessary to produce a high cyclohexane solubility. For Wyodak coal and Illinois #6 coal, the H/C and  $H_{al}/H_{ar}$  ratios of the extracts decreased as the cyclohexane solubilities increased. The H/C ratios of all the extracts were always

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\*M.S. Thesis

substantially higher than that of the parent coal. Soxhlet extractions with pyridine of the residues from Wyodak coal and Illinois #6 coal indicated that zinc chloride also increased the asphaltene and preasphaltene content of the coal.

Studies with co-catalysts indicated that Zn metal, NiS, and  $\text{AlCl}_3$  in combination with zinc chloride were all incapable of increasing the yield of oil like products. In contrast, Ni metal acted more favorably and increased yields were obtained using Ni/ $\text{ZnCl}_2$  catalyst mixtures. Methanol, ethanol, and isopropanol additives in the presence of zinc chloride increased the solubility of coal in cyclohexane. However, at least a part of this increase must be ascribed to alkylation of the coal structure. Finally, t-butanol was found to lower the yield of cyclohexane soluble products.

Further studies of the zinc chloride-coal system revealed that pre-impregnation of the catalyst into the coal from methanol solution was unnecessary and that catalyst to coal contacting did not limit the rate of reaction. Studies on the effect of solvent volume indicated that increasing the solvent/coal ratio had no effect on the reaction yield. Finally, the use of benzene as the extracting solvent resulted in higher yields of extractable products, exhibiting lower H/C and  $\text{H}_{\text{al}}/\text{H}_{\text{ar}}$  ratios compared to cyclohexane extracts. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48.

To my wife, Saadia,  
for her encouragement and understanding



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## I. INTRODUCTION

Coal derived liquids may in the future serve as substitutes for petroleum which is in increasingly short supply. The U.S. has over a quarter of the world's known reserves of coal, but direct utilization of this abundant energy source presents difficulties in terms of solids handling and air pollution. Several approaches have been proposed for conversion of coal to clean liquid products and several coal liquefaction processes are currently under advanced stages of development. While these processes will serve as the basis for first generation technology, there still exists a need for more economically attractive approaches.

Research to improve and further develop coal liquefaction processes will continue to play an important role in shaping the future of this new industry. One such area of current investigation by several research organizations is the use of zinc chloride as a possible coal liquefaction catalyst. The present study was initiated with a similar objective and was specifically aimed at investigating the solubilization of several different types of coals in the presence of zinc chloride, with and without co-catalysts and additives.

This chapter briefly discusses coal chemistry and summarizes several coal liquefaction processes approaching commercialization. The use of zinc chloride as a possible coal liquefaction catalyst is discussed, and finally, the objective and scope of this research are presented.

### A. Coal Chemistry

In order to study coal liquefaction, it is important to gain some understanding of the chemical and physical characteristics of coal. It is generally agreed that coal is a very complicated network of organic species with the bulk of the coal material being porous in its natural form. This polymeric network originate primarily from the decomposition of plants. The original plant material consisted of highly ordered polymers such as cellulose and lignin, but as degradation occurred, the lighter hydrogen rich substituents were released and the resulting residue took the form of a hydrogen depleted and highly disordered macromolecular substance. As these changes occurred, the carbon content increased, the oxygen content decreased, and the calorific value at each step continued to increase with age. Thus, the original plant material is converted sequentially to humic acid, peat, lignite, sub-bituminous coal, bituminous coal, and finally to anthracite (1,2,3,4).

Various chemical characterization methods have been utilized by researchers to gain more insight into the structure of coal. Among these have been (1) elemental analysis, (2)  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR, (3) chemical analysis of functional groups and (4) polarography. Many of these are destructive of the original coal structure. Recently, Pines (5) at the University of California at Berkeley has developed a method referred to as solid state CP $^{13}\text{-C}$ , which provides information concerning the aliphatic and aromatic

portions of coal without requiring chemical or physical changes in the structure before analysis.

Researchers (6,7,8,9) have concluded that the coal network consists of varying amounts of aromatic and hydro-aromatic structural units. Since ring fusion and cross-linking increase as coalification progresses, the aromatic content varies from about 40 to 50% for sub-bituminous coal to over 90% for anthracite. The aromatic and hydroaromatic structures are in turn linked by two major types of bridges mainly (1) short aliphatic chains and (2) ether linkages. The cleavage of these linkages and the termination of the fragments with hydrogen are important processes which occur during coal liquefaction.

The hydrocarbon chain represents the backbone of the coal structure but several major functional group types have also been identified in coal. Oxygen occurs mainly as phenolic or ether groups with lesser amounts of carboxylic acid and esters. Sulfur has a chemistry very similar to that of oxygen, with major groups such as sulfides and thiophenes. Nitrogen occurs predominantly as pyridine or pyrrolic type rings. Finally, metals are found mainly as salts or are associated with porphyrins. During coal liquefaction processing, all these functional groups change depending on the severity of the operation.

#### B. Coal Liquefaction Processes

Various coal liquefaction processes are currently under development. Most of these can be classified into three

general categories: (1) Pyrolysis, (2) Fischer-Tropsch Synthesis, and (3) Dissolution.

Pyrolysis processes are based on the thermal decomposition of coal by heating it in the absence of oxygen to drive off volatile matter. This produces a liquid product as well as by-product gas and char. After separation into gaseous and liquid products, the gases are freed from unwanted substances such as sulfur. The overall product is both a usable gas and a usable liquid. The char can be used to produce hydrogen for hydrotreating the liquid products or it may be burnt to produce the necessary heat for pyrolysis. Pyrolysis processes will probably not be a major source of synthetic petroleum because these methods yield a low volume of liquids.

Fischer-Tropsch synthesis is an indirect method for producing liquid fuels from coal and in concept combines two major steps. The first is the production of synthesis gas ( $\text{CO} + \text{H}_2$ ) from coal or coke. In a second step this gas is then catalytically converted to hydrocarbons. The Fischer-Tropsch synthesis method produces a complex product mixture which must be highly processed to obtain a high octane gasoline.

Dissolution is the third major class of liquefaction processes. In this type of processes the crushed or ground coal is dissolved in a solvent, the ash is removed, and the resulting oil is upgraded by hydrocracking to produce a synthetic crude. Subsequently, the remaining solid can be used for generation of the hydrogen needed for the process.



Two types of dissolution process exist: (1) processes that use hydrogen but no catalyst such as the SRC Process of the Pittsburgh Midway Coal Company, and (2) processes that use both hydrogen and a catalyst such as the H-Coal Process of the Hydrocarbon Research Company.

At this time and stage of development, the three processes which have progressed the furthest towards commercialization are (1) the Exxon Donor Solvent process, (2) the H-Coal process, and (3) the SRC-II processes. All three are classified within the dissolution class of coal liquefaction processes and involve dissolving the coal in a coal derived solvent and then converting the separated liquid into low molecular weight petroleum feedstock by hydrogenation. The products from all three processes have a wide range of boiling points and could produce gasoline, diesel, gas-oil fractions, and residual oil for electric power generation. In addition, the necessary hydrogen required for hydrogenation to upgrade the liquid could be produced from the carbon rich solid residue derived from each process (10). A brief description of each of the above process follows.

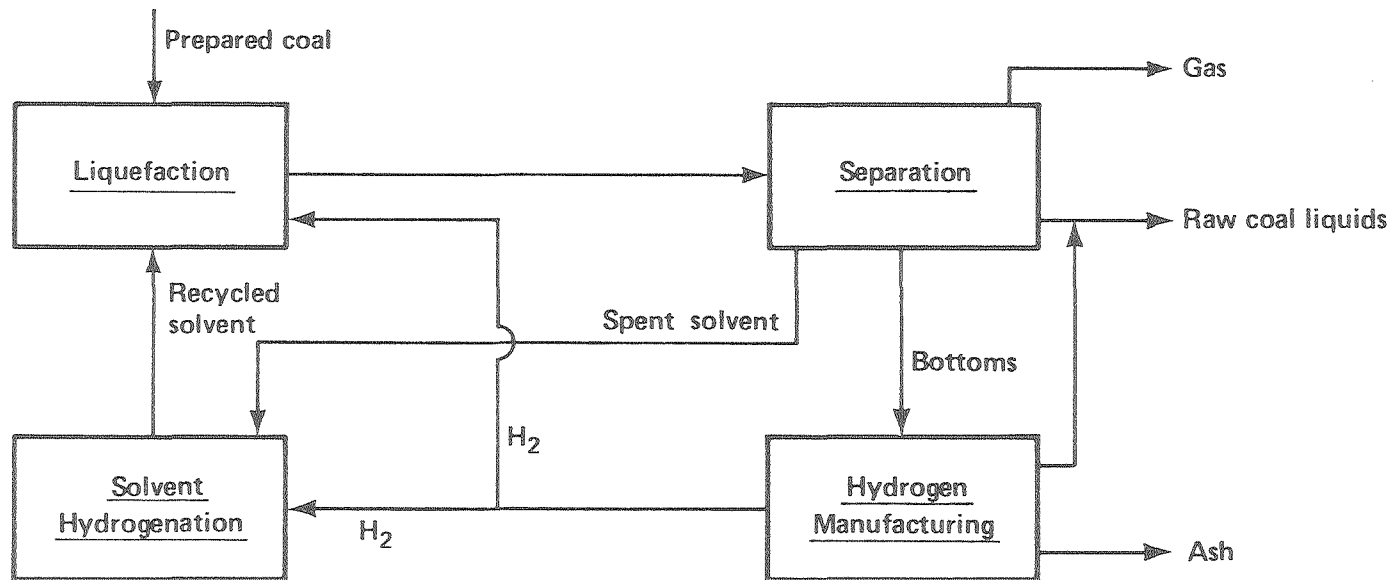
The Exxon Donor Solvent (E.D.S.) process uses coal conversion steps that involve engineering and design technology similar to that practiced in the petroleum industry (11,12). This indirect catalytic hydrogenation process can produce low sulfur liquid fuel without utilization of mechanical separation devices or solids-tolerant catalysts. The E.D.S. process has already been

demonstrated at a 1 t/d pilot scale, and plans for a 250 t/d pilot plant are currently in progress.

The Exxon process consists of four major processing steps as illustrated in Figure 1-1. The coal, recycled solvent, and hydrogen are first reacted in the liquefaction block. Thereafter the resulting products are separated in the separation block to produce gas, recycled solvent, raw coal liquids, and a heavy bottoms stream that consists of the unreacted coal and mineral matter. The recycle solvent is catalytically hydrogenated using multimetallic catalysts in the solvent hydrogenation block and then recycled back to the reactor. Finally, the heavy bottoms from the separation block are further processed to produce additional liquids and hydrogen or fuel gas in the hydrogen manufacturing block. Gas produced from the process is also used as fuel and for hydrogen manufacturing.

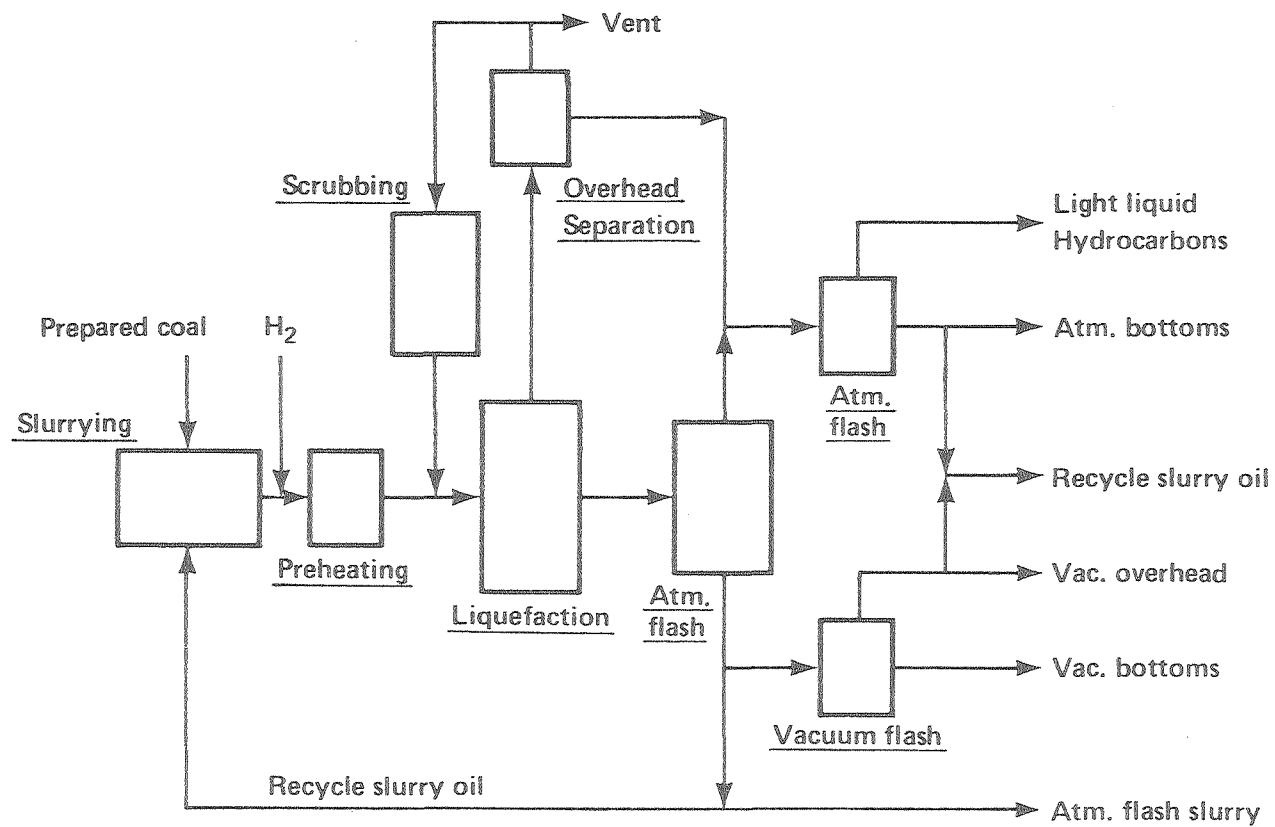
The Hydrocarbon Research Inc. (HRI) has developed the H-Coal process which uses direct catalytic hydrogenation (13). The H-Coal process has progressed through a 3 t/d process development unit scale and construction is currently in progress to demonstrate the process at a 250 t/d scale.

In the H-Coal process, crushed coal is mixed with recycled oil to form a slurry which is pumped with hydrogen into a preheater operating at 2700 psig (see Figure 1-2). The slurry-gas mixture then enters the reactor, which can be characterized as an ebullated catalyst column operating at 450°C and 2700 PSI. The catalyst, cobalt molybdate,



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Figure 1-1. Schematic of the Exxon Donor Solvent Process for Coal Liquefaction



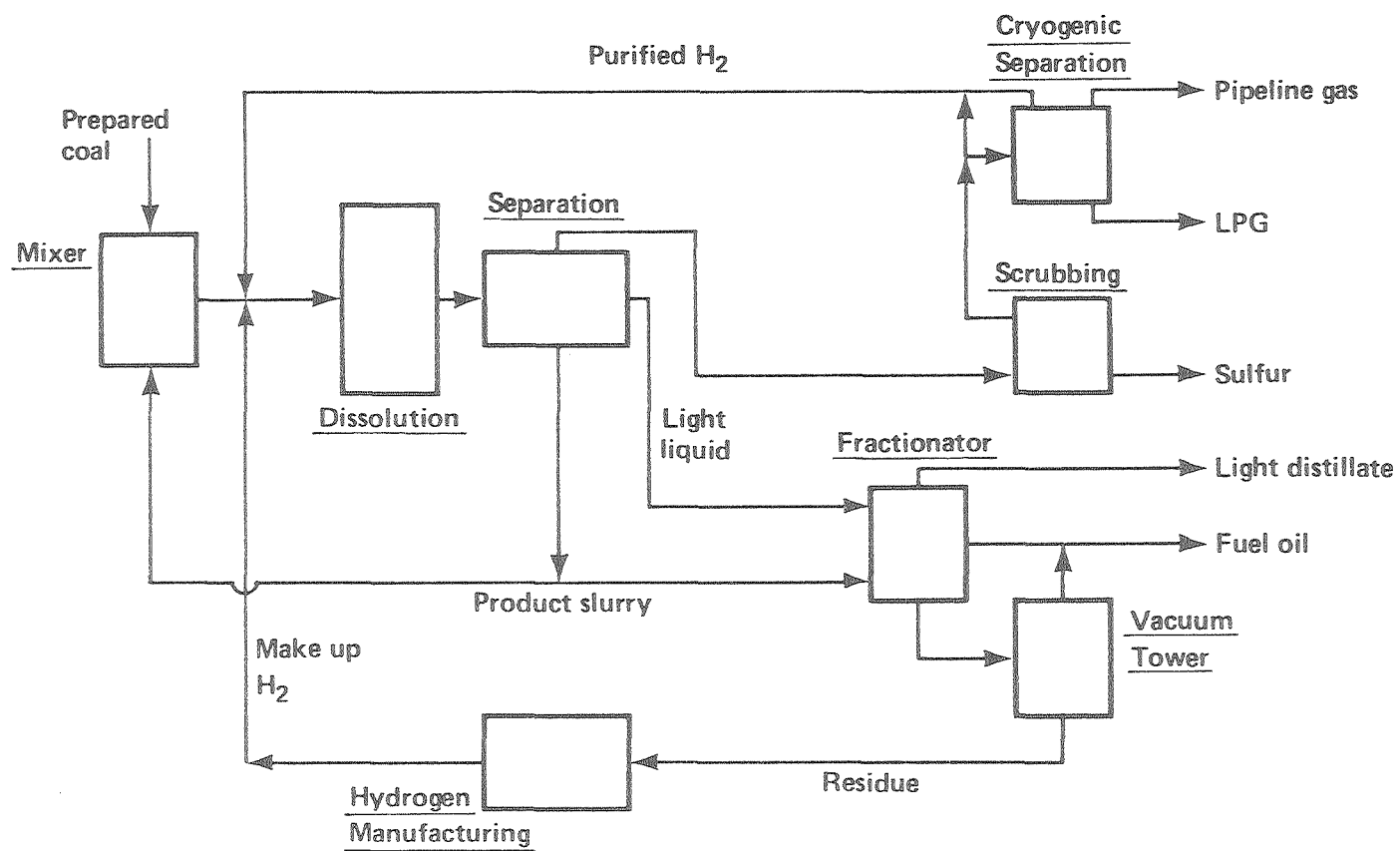
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Figure 1-2. Schematic of the H-Coal Process for Coal Liquefaction

settles out in the bed at a point below which the hot liquid product is drawn into an atmospheric flash drum. After further separations, various synthetic crude fractions are obtained which must be subjected to further refining and upgrading. The char, containing the unconverted solid, can be used as a fuel or be subjected to pyrolysis to obtain more liquid products.

The third process approaching commercialization is the Solvent Refined Process II (14,15), in which the coal is treated at an elevated temperature in the presence of a hydrogen donor solvent and hydrogen gas but no added catalyst. The SRC-II process evolved from the SRC-I process. The earlier process was designed to lower the sulfur content of coal, remove mineral matter, and convert the coal into a low melting solid which could be solubilized in simple organic solvents. This solvent refined coal had utility as a substitute clean coal or boiler fuel. Further work led to the development of the SRC II process in which the primary product is an ashless distillate fuel containing less than 0.4% sulfur, in contrast to the solid fuel produced in the original version of the SRC I process. Additional products of the SRC II process include pipe line gas, LPG, a light distillate liquid  $C_5$ -400 F, phenols, and ammonia. The SRC II process is presently being demonstrated at a 50 t/d pilot plant.

A schematic flow diagram for the SRC II process as visualized by its developers is given in Figure 1-3. Raw coal is pulverized and dried in the coal preparation area,



XBL 796-2012

Figure 1-3. Schematic of the SRC-II Process for Coal Liquefaction

and subsequently mixed with process derived slurry solvent. This slurry together with hydrogen is pumped to a reactor where hydrocracking of the dissolved coal to lower molecular weight material occurs. The reactor effluent then goes to a hot high pressure separator. The overhead vapor from the separator is cooled and separated into LPG and pipeline gas. The residue from the high pressure separator, after being flashed to lower pressure, is split into two major streams. The first stream is returned to the reactor and comprises the recycled solvent. The second stream is returned to the fractionator and vacuum tower for separation of major products in the process. Subsequently, the bottoms from the vacuum tower, containing the undissolved mineral residue and the residue of the undissolved coal, go to a gasification facility for conversion to hydrogen. By comparison with the original SRC-I process, the SRC-II process yields a larger conversion of the dissolved coal and eliminates the need for mineral residue drying and product solidification.

#### C. Coal Liquefaction Using Zinc Chloride

Coal researchers generally agree that first generation coal liquefaction processes will depend heavily on conventional catalysts systems, such as cobalt molybdate. However, in order to improve the economics of coal derived liquids, it will be necessary to lower the extreme processing conditions presently being utilized in coal liquefaction processes. To do this it will be desirable to develop more catalysts capable of affecting liquefaction at lower temperatures and pressures.

Metal halides are potentially attractive second generation catalysts and have a demonstrated activity for coal liquefaction. Among the various metal halides, zinc chloride is of special interest. Zinc chloride is molten at reaction conditions and this in turn serves to overcome some of the problems inherent in heterogeneous catalysis. Additional advantages of using zinc chloride include minimal hydrogen usage and the possibility of catalyst recoveries exceeding 99%. In view of these advantages of zinc chloride, work has been conducted by various research groups at both fundamental and applied levels (16,17,18,19,20,21). These investigators have not only enhanced the level of understanding of zinc chloride as a coal liquefaction catalyst but have also developed pilot processes utilizing zinc chloride as the principal catalyst.

1. Chemical Reaction related to coal liquefaction promoted by Zinc Chloride

Extensive work has been conducted in the Chemical Engineering Department of the University of California at Berkeley to study the catalytic effects of zinc chloride on both coal (16,17,18) and coal model compounds. The work on coal model compounds by Bell and his associates (22,23,24) has served to explain the role of zinc chloride in affecting selective cleavage and subsequent hydrogenation of model compounds containing structural units present in coal.

Model compound work by Mobley and Bell (23) showed that ether and sulfide linkages are cleaved in the presence of zinc chloride. This study revealed that the linkages of the



type  $\text{ArCH}_2\text{-O-CH}_2\text{Ar}$  cleave and water is formed with the elimination of the oxygen. In contrast, the study showed that linkages of the type  $\text{Ar-O-CH}_2\text{Ar}$  will cleave but the oxygen will remain in the form of a phenol.

The study on aliphatic bridges by Taylor and Bell (24) indicated that the cleavage of linkages between aromatic units depended on the nature of the aromatic nuclei. Thus, naphthyl and hydroxyphenyl groups were more easily cleaved from the aliphatic linkages than phenyl groups. This study showed that  $\text{ZnCl}_2$  could not cleave aliphatic bridges between single unsubstituted phenyl rings nor cleave aryl-aryl bonds. However,  $\text{ZnCl}_2$  was successful in cleaving linkages connecting aromatic nuclei with hydroxyl substituents. In addition replacement of the phenyl group by a naphthyl group also increased the ability of the  $\text{ZnCl}_2$  to cleave the aliphatic linkages.

Finally, a study by Salim and Bell (22) on fused ring clusters has shown that hydrogenation and cracking of such structures require very strong Lewis acids such as  $\text{AlCl}_3$  and that these structures do not readily react in the presence of zinc chloride.

## 2. Process Development Work

Work has also progressed toward the development of several coal liquefaction processes using zinc chloride as the principal catalyst. Two such major applications of zinc chloride have been the work conducted by the Consolidation Coal Company (Consol), which has been continued by Conoco

Coal Development Company, and work performed by the University of Utah. The work at Consol has stressed the use of massive amounts of zinc chloride while the investigators at the University of Utah have used small amounts of zinc chloride.

The work at Consol (3,25,26,27,19) using zinc chloride has extended over two decades and covered the application of this catalyst system to both coal extracts and various coal substrates. By using massive amounts of the metal halide catalyst, single stage conversion of coal into high octane gasoline was accomplished at temperatures around 425°C and pressures up to 4200 psig with 60 minute reaction time. Major efforts are presently underway by Conoco to develop a 1 t/d Process Development Unit for the conversion of coal to distillate fuel. Conoco estimates that zinc chloride processing will save 8 to 16% of cost over ebullated bed hydrocracking, hydrotreating, and reforming as conducted in the H-Coal process.

Since zinc chloride recovery is a prime requirement for the process to be economically feasible, Conoco has devoted some effort to regenerate the spent melt from their continuous coal hydrocracking bench scale units (27). One of the techniques involves the combustion of the spent melt with air in a fluidized bed of inert solids. This fluidized bed process removes the carbon, nitrogen, and sulfur impurities from the melt and simultaneously vaporizes the zinc chloride, which is thereafter condensed and recycled

back to the hydrocracking reactor. Zinc chloride recoveries of up to 99.6% have been reported.

At the University of Utah (28), dry powdered coal has been impregnated with about 5% zinc chloride and reacted in small diameter tubes at reaction temperatures of 500°C and a hydrogen pressure of 1800 psig. The resulting liquids were determined by the investigators to be principally aromatic in nature. This process has progressed through several bench scale phases, all of them being directed toward a short contact time, high ratio of hydrogen to coal, no solvent, and minimal zinc chloride usage.

The investigators at the University of Utah have also devoted great effort toward the recovery of zinc chloride catalyst from the spent melt (29). According to this group of researchers, about 1/3 of the zinc was present in the liquid phase while the rest stayed with the char. A water wash was used to recover the catalyst in the liquid phase, and the separation was easily achieved. However, removal of zinc chloride from the char was more difficult and required HCl acid washes in addition to the water wash to obtain 70% of the catalyst present. The remaining amount of the zinc chloride was retained in the organic matter within the char and a room temperature nitric acid leach was necessary to remove the remaining zinc. Overall, the researchers reported 98.5 to 99.7% zinc recoveries with a water, HCl, and HNO<sub>3</sub> wash procedure.

#### D. Objective and Scope

The objective of this investigation was to study the solubilization of SRC-I, Wyodak sub-bituminous coal, and Illinois #6 coal in the presence of zinc chloride, with and without co-catalysts and additives. The experimental program was conducted in three major phases:

1. The first phase consisted of collecting rate data on the usage of zinc chloride as a coal liquefaction catalyst. The rate data included the effect of catalyst loading, reaction time, temperature, and pressure.

2. The second set of experiments were conducted to study the effect of co-catalysts and additives, in conjunction with zinc chloride, with the aim of promoting the conversion of coal to oil-like products.

3. The third and final phase of the investigation was conducted to study the effect of physical changes in the reaction procedure with the anticipation that these might improve the degree of coal conversion to soluble products.

All coal liquefaction experiments conducted in this study were accomplished in the presence of an extracting solvent medium. This approach is similar to that described by Tanner and Bell (18).

The use of an extracting solvent provides several advantages in conducting the coal liquefaction reactions:

1. Continuous removal of the oil-like products from the unreacted products in order to prevent condensation and polymerization of the products.

2. Selectivity in the type of products being separated from the rest of the coal material.

3. Minimal solvent incorporation into the coal unlike the case with donor solvents.

4. Good solvent penetration into the pore structure of the coal.

## II. EXPERIMENTAL APPARATUS AND PROCEDURES

The purpose of this chapter is to describe the experimental equipment used in this study, to outline briefly the source and purity of the materials used, and to describe the procedures utilized to conduct the reactions and characterize the resulting products.

### A. Experimental Equipment

An experimental system consisting of a batch reactor capable of operating at high temperature and high pressure was utilized during the research program. The system was complete with all necessary instrumentation and controls to provide accurate operating data and adequate control during the course of the experiments.

#### 1. Summary of Reactor System

Basically the reactor system consisted of a 300 cm<sup>3</sup> batch autoclave, a gas flow system to introduce the desired gas into the reactor, and necessary instrumentation to monitor and control the progress of the reaction. A schematic of the reactor system is given in Figure 2-1.

The reaction system was located and operated in an explosion proof bay in order to protect the operator and surrounding personnel. The majority of the control apparatus was operated from outside the bay, thus minimizing the presence of the operator in the autoclave room.

#### 2. Reactor Description

The autoclave was a 300 cm<sup>3</sup> unit, Model ABP-300, manufactured by Autoclave Engineers, Inc., of Erie,

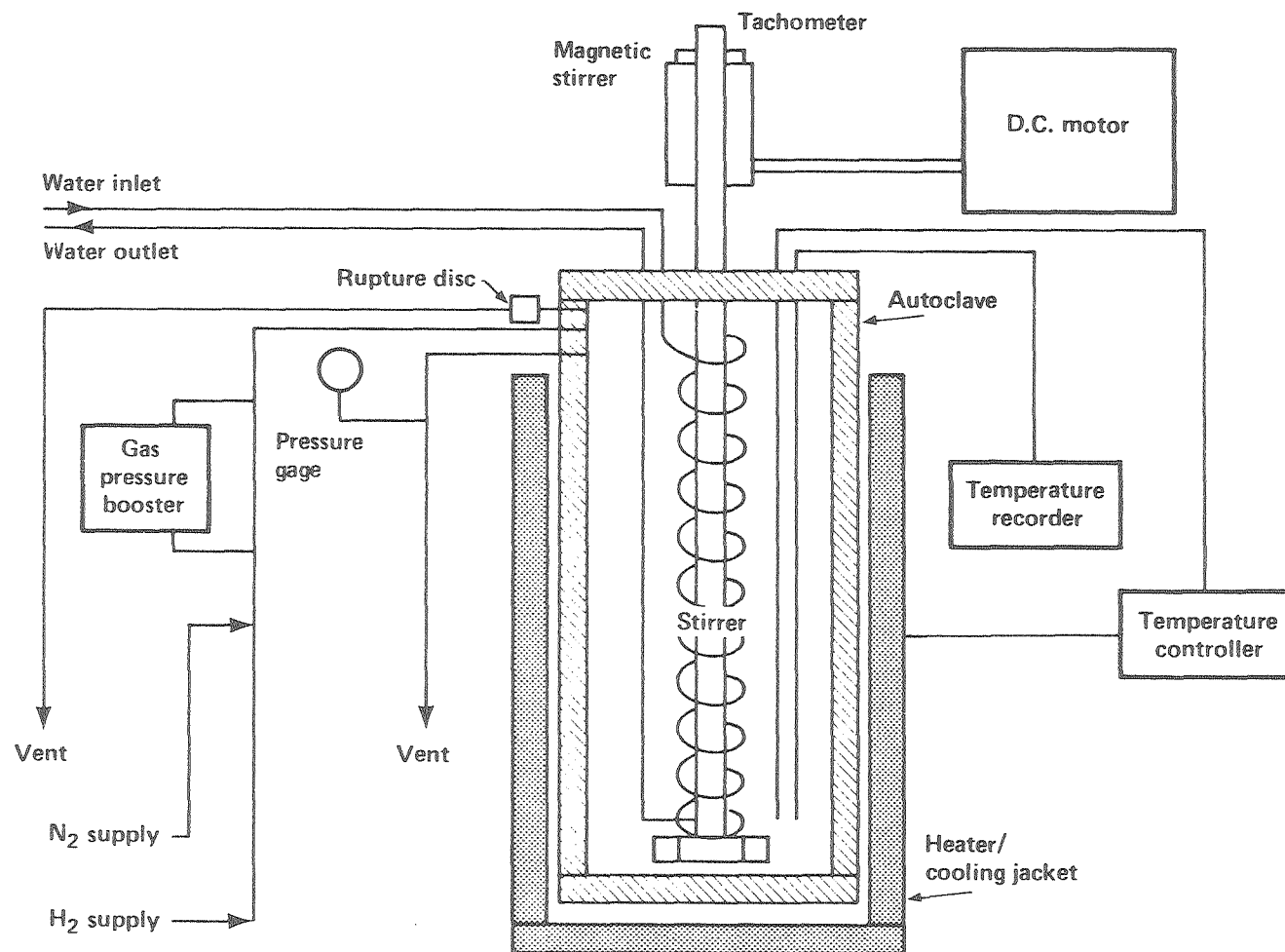


Figure 2-1. Experimental Apparatus

Pennsylvania. The unit was constructed of 316 stainless steel and was rated at 5000 psig at 350°C. The reactor was equipped with a magnetically driven stirring assembly capable of operation up to 1200 RPM. This stirring assembly consisted of a shaft-propellor combination immersed in the core of the unit to provide adequate agitation of the reactants.

Heating of the autoclave was accomplished by the use of an electrical resistance heater which fitted concentrically around the outside of the reactor core. Cooling of the reactor was provided by cooling coils immersed in the reaction zone of the autoclave. Additional secondary cooling was provided by a cooling jacket which could be manually substituted for the heater around the reactor body during the cooling cycle of the reaction.

### 3. Gas Flow System

The autoclave system was connected to gas cylinders containing  $H_2$  and  $N_2$  gas. Two flow systems were available depending on the gas pressure required inside the reactor. One system consisted of a direct connection between the supply gas cylinder and the reactor, which allowed the maximum initial pressure attainable in the reaction zone to be equivalent to the supply gas cylinder pressure. In cases when higher initial pressure was necessary, a secondary flow system was activated which allowed the gas to flow to a booster pump assembly where the pressure was raised in excess of the supply pressure before introduction into the autoclave.



For safe operation, the autoclave was equipped with a rupture seal in order to vent the gas out of the system in case of excessive internal pressure. This rupture seal assembly was vented to the atmosphere outside the explosion-proof bay.

#### 4. Auxiliary Instrumentation and Control

In order to monitor and closely control the reaction conditions, necessary instrumentation was provided to measure operating variables such as temperature and pressure inside the reaction zone.

Control instrumentation consisted of a Honeywell Automatic Temperature controller which allowed the reaction to proceed at the desired temperature set by the operator. In addition, a Leeds and Northrup Speed Temperature recorder was installed which enabled continuous temperature recording. The two temperature measurements were independent of each other and provided for a check on each other.

The pressure inside the system was monitored by a Bourdon type pressure gauge manufactured by the U.S. Gauge Company. Additional gauges and indicators monitored the rotational speed of the stirrer unit, flow of cooling water to the reactor, and status of the reactor heating system.

#### B. Materials

During the course of this study several substrates were utilized. These included Solvent Refined Coal (SRC-I), Wyodak sub-bituminous coal, and Illinois #6 bituminous coal. The SRC-I was refined and supplied by the Pittsburgh and Midway Coal Mining Company's demonstration plant at Tacoma,

Washington. The Wyodak coal was obtained from the Roland top seam of the Wyodak Corporation's mine at Gillette, Wyoming. The Illinois #6 coal was supplied by the Illinois Geological Survey. Table 2-1 summarizes the ultimate elemental composition of these three different substrate materials.

The principal catalyst utilized was zinc chloride, but several cocatalysts were explored in order to enhance the zinc chloride activity. Table 2-2 gives a brief outline of the source and purity of the different catalysts used in this study.

Cyclohexane was the prevalent solvent used as the extracting medium, however various additives were used as promoters and alkylating agents. These are also described briefly in Table 2-2.

### C. Experimental Procedures

#### 1. Reaction Procedures

The reaction procedure consisted of four main steps.

1. Preparation of the substrate and catalyst.
2. Loading of reactants and catalyst into the reactor.
3. Conducting the reaction.
4. Product retrieval.

The first step consisted of grinding the substrate to the desired particle size which was accomplished in a laboratory rod mill. The SRC substrate was reduced to -100 mesh while both the coal substrates were ground and subsequently sieved to -60 mesh and +200 mesh. The grinding was conducted in bulk amounts and the contents were stored under nitrogen. Approximately 18 hours before a planned reaction,

TABLE 2-1

Ultimate Analysis of Solvent Refined Coal, Wyodak Coal,  
and Illinois #6 Coal

Type of Coal Component	SRC-1	Wyodak	Illinois #6
Carbon	87.13	62.57	64.30
Hydrogen	5.61	5.00	4.47
Nitrogen	2.20	0.92	1.33
Sulfur	0.53	1.20	4.35
Ash	0.20	14.09	16.68
Oxygen	4.33	16.22	8.87

Notes:

(i) Wyodak and Illinois #6 coal were analyzed by  
Commercial Testing and Engineering Co., Denver, Colorado.

(ii) Solvent Refined Coal was analyzed by the  
Microanalysis Laboratory of the College of Chemistry of  
the University of California at Berkeley.

(iii) Oxygen was determined by difference.

TABLE 2-2

## Summary of Catalysts, Solvents, and Additives

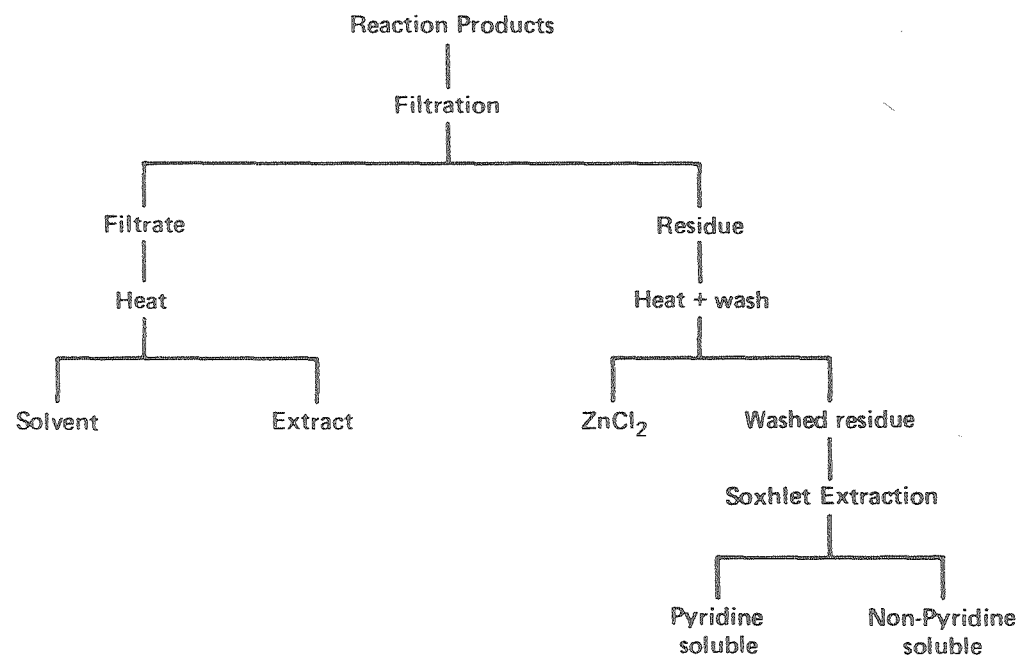
MATERIAL	SUPPLIER	PURITY, %
I. Catalysts		
1. $\text{ZnCl}_2$	Mallinckrodt	97.0
2. $\text{AlCl}_3$	Mallinckrodt	99.5
3. Zinc metal (30 M)	M.C. & B	-
4. Nickel (200 M)	M.C. & B	-
5. NiS	Research Organic	90.0
II. Solvents		
1. Cyclohexane	M.C. & B	99.0
2. Benzene	Mallinckrodt	99.0
III. Additives		
1. Methanol	Mallinckrodt	99.5
2. Ethanol	Mallinckrodt	99.5
3. Isopropanol	Mallinckrodt	99.8
4. t-Butanol	Mallinckrodt	absolute

the desired amount of substrate was removed from the storage container and heated to 105°C in a nitrogen purged vacuum oven to drive out the moisture. The zinc chloride catalyst was similarly dried overnight and used the following day without further pretreatment. On the day of the reaction, the substrate and the catalyst were weighed and placed inside a glass liner.

During the second step, the glass liner was loaded into the reactor, which was then sealed. The air in the reactor was flushed out, and the system was pressurized with hydrogen. The autoclave was then heated up to the desired temperature.

On reaching the desired temperature (and pressure), the reaction was allowed to proceed in a batch form for the desired length of time. All operating variables were monitored closely during the experiment. At the conclusion of the run, the system was quenched and cooled down to ambient conditions.

The handling of reaction products is outlined in Figure 2-2. The products were first filtered through a medium frit Buchner funnel, to give a liquid product (filtrate) and a corresponding solid phase (residue). The solvent was completely evaporated off from the filtrate by placing it on a hot plate, and the resulting extract represented the solvent soluble portion of the products. Thereafter, both the extract and the residue were dried in a vacuum oven at 105°C and then stored separately in glass vials for further characterization.



XBL 796 - 2008

Figure 2-2. Product Separation Procedures

## 2. Characterization Methods

### a. Percent Cyclohexane Solubility

The percent of the original coal soluble in cyclohexane and retained as the extract was determined by dividing the weight of the extract by the initial moisture and ash free weight of the substrate. This extract cut represented a measure of the conversion of coal to oil like products (6,1).

### b. Proton Nuclear Magnetic Resonance

Proton nuclear magnetic resonance  $^1\text{H}$ -NMR was utilized to determine the ratio of aliphatic hydrogen to aromatic hydrogen in the extract. Approximately 100 mg of the extract was dissolved in  $\text{DCCl}_3$  spiked with 1% TMS, and a spectrum was obtained using a 60 MHz Varian Model T-60 NMR spectrometer. Integration over the aliphatic region and the aromatic region provided approximate distribution of the aliphatic hydrogen and aromatic hydrogen present in the extract.

The  $^1\text{H}$ -NMR spectrometry (19, 30, 31, 32, 33, 34) provided a direct means for studying the hydrogen distribution present in the cyclohexane soluble material. This technique is superior to other analytical techniques since all protons have essentially the same NMR sensitivity, and therefore no intensity calibration of the spectrometer is required.

The  $^1\text{H}$ -NMR spectra of coal extracts do not give the sharply defined spectra characteristic of pure compounds but, rather, yield a broad and diffuse envelope, due to the large range of chemical shifts and to the existence of complex

spin-spin couplings. The basis for quantitative analysis of such spectra lies in the fact that the absorption band characteristics of different functional groups are sufficiently separated from each other. The assignment of absorption areas to different hydrogen types have been conducted by various investigators and is summarized briefly as follows:

$\delta$  (ppm)

- |     |                    |   |
|-----|--------------------|---|
| 9-6 | $H_{ar}$           | - Hydrogen in aromatic and phenolic groups                                    |
| 4-2 | $H_{\alpha}$       | - Hydrogen in saturated groups alpha to aromatic rings.                       |
| 2-0 | $H_{\beta+\gamma}$ | - Hydrogen in saturated groups beta and gamma or further from aromatic rings. |

The aromatic protons band ( $H_{ar}$ ) is broad, diffuse and of rather low intensity due to the small number of aromatic protons present in the cyclohexane soluble extract. The  $H_{\alpha}$  band contains methylene alpha to two rings and also contains many other structural types of protons including those adjacent to heteroatoms. The  $H_{\beta+\gamma}$  band correspond to protons in saturated groups which are beta, gamma, or further away from an aromatic ring. In this study the ' $H_{ar}$ ' notation corresponds to the  $H_{ar}$  band, while the ' $H_{al}$ ' notation corresponds to the  $H_{ar}$  band, while the ' $H_{al}$ ' symbol represents the sum of the  $H_{\alpha}$  and  $H_{\beta+\gamma}$  bands.

The Brown and Ladner equation (32) was used to determine the aromaticity factor in order to deduce information concerning the carbon distribution from the  $^1H$ -NMR data. The simplified version of the Brown and Ladner equation as utilized in this study is given as follows:



$$f_a = \frac{C/H - \frac{H_{al}/H_{ar}}{(H_{al}/H_{ar}) + 1} \cdot (C/H)_{al}}{C/H}$$

where

$f_a$  = Aromatic carbon/total carbon

$C/H$  = Elemental carbon/hydrogen ratio from the maf analysis of material under analysis

$H_{al}/H_{ar}$  = Aliphatic hydrogen/aromatic hydrogen ratio of material under analysis as determined from the  $^1H$ -NMR

Several assumptions were made by Brown and Ladner in the application of this equation, and the result of the calculation depends upon an assumed knowledge of  $(C/H)_{al}$ , the carbon to hydrogen ratio in various non-aromatic groupings (assumed 0.5 in the study). The equation, however, has yielded important results to numerous investigators when applied to a great number of carbonaceous materials such as petroleum asphaltenes, coal asphaltenes, and coal tar pitches (32).

### c. Elemental Analysis

Elemental analysis was performed on both the extract and the residue by the Microanalysis Laboratory of the College of Chemistry of the University of California at Berkeley. The carbon, hydrogen, and nitrogen analysis was obtained using standard combustion techniques utilizing a Perkin Elmer Model 240 CHN Analyzer.

In order to obtain the sulfur content, the samples were combusted at 900°C to form  $SO_2$ , which was then separated by

a  $\text{H}_2\text{O}_2$  solution, and finally precipitated with  $\text{BaCl}_2$  to form  $\text{BaSO}_4$ . The sulfur content was then determined gravimetrically from the amount of  $\text{BaSO}_4$  formed.

Similarly the chlorine was determined by combustion at  $900^\circ\text{C}$  to form  $\text{Cl}_2$ , which was adsorbed by a  $\text{H}_2\text{O}_2$  solution. The resulting solution was then titrated with  $\text{AlNO}_3$  to give the percent chlorine in the sample.

Metal analysis was conducted by the Microanalysis Laboratory by atomic absorption in a Perkin Elmer Model 360 Atomic Absorption Spectrophotometer. After destruction of all organic matter by concentrated sulfuric acid and 30%  $\text{H}_2\text{O}_2$ , the resulting solution was run on the spectrophotometer to give absorbances, which were compared with known standards to give the percent of a particular metal present in the sample.

#### d. Soxhlet Extraction

In order to obtain some characterization of the non-cyclohexane soluble residue, Soxhlet extractions were carried out using pyridine as the extracting solvent. Since pyridine dissolves oils, asphaltenes, and preasphaltenes, the Soxhlet extraction data presented some indication of the effect of the reaction on the asphaltenes and preasphaltenes. The residues were first washed with three aliquots of 250 ml of distilled water at  $90^\circ\text{C}$  in order to remove the zinc chloride. Standard Soxhlet equipment and procedures were then utilized in conducting extraction of a known weight of the washed residue. On completion of the extraction, the

percent pyridine solubility was calculated on the basis of the amount of residue dissolved in the pyridine. Corrections were applied to account for pyridine addition to any zinc chloride remaining in the residue.

### III. RESULTS AND DISCUSSION

The purpose of this investigation was to study the use of zinc chloride as a coal liquefaction catalyst in an extracting solvent medium. In order to accomplish this goal, experimental work was conducted and is reported in this chapter in three different phases:

1. Rate data on the useage of zinc chloride as a liquefaction catalyst for Wyodak coal, Illinois #6 coal, and SRC-I.

2. The effects of co-catalysts and additives, which would promote the conversion of coal to oil-like products, in conjunction with zinc chloride.

3. The effects of improved coal-catalyst contacting and use of different solvents and amounts.

#### A. Rate Data

During this phase of the research program, experiments were conducted to study the effect of various experimental variables such as catalyst loading, reaction time, reaction temperature, and hydrogen pressure. These experiments were conducted using zinc chloride in the absence of any additives.

1. Catalyst Loading

Table 3-1 and Figure 3-1 show the effect of catalyst loading on the solubility of Wyodak Coal and the characteristics of the product. The data show that as the catalyst/coal weight ratio is increased from 0 to 0.6, the solubility of the coal in cyclohexane increases from 6.9% to 20.0%. Increasing the catalyst/coal weight ratio from 0.6 to 1.0

TABLE 3-1

Effect of Zinc Chloride Loading on Reaction Using Wyodak Coal

T = 300°C  
 P = 2000 psig  
 Tim = 60 min

Coal = 5 g  
 Catalyst = Zinc Chloride  
 Solvent = 70 ml Cyclohexane

Run No.	Catalyst wt, g	Cat/Coal Ratio	Sol., % maf	Extract Analysis		<sup>1</sup> H-NMR Data	
				H/C	N/C	H <sub>al</sub> /H <sub>ar</sub>	f <sub>a</sub>
69	0	0	6.9	1.44	0.0054	> 10.0	-
56	1.25	0.25	13.0	1.39	0.0016	8.9	0.37
58	2.2	0.44	18.0	1.29	0.0014	8.3	0.42
54	2.5	0.50	19.3	1.28	0.0016	8.6	0.43
59	3.0	0.60	20.0	1.29	0.0015	7.0	0.44
57	3.75	0.75	14.8	1.34	0.0020	6.6	0.42
25	5.0	1.0	13.5	1.33	0.0015	7.5	0.41
52	15.0	3.0	12.3	1.30	0.0012	7.6	0.42

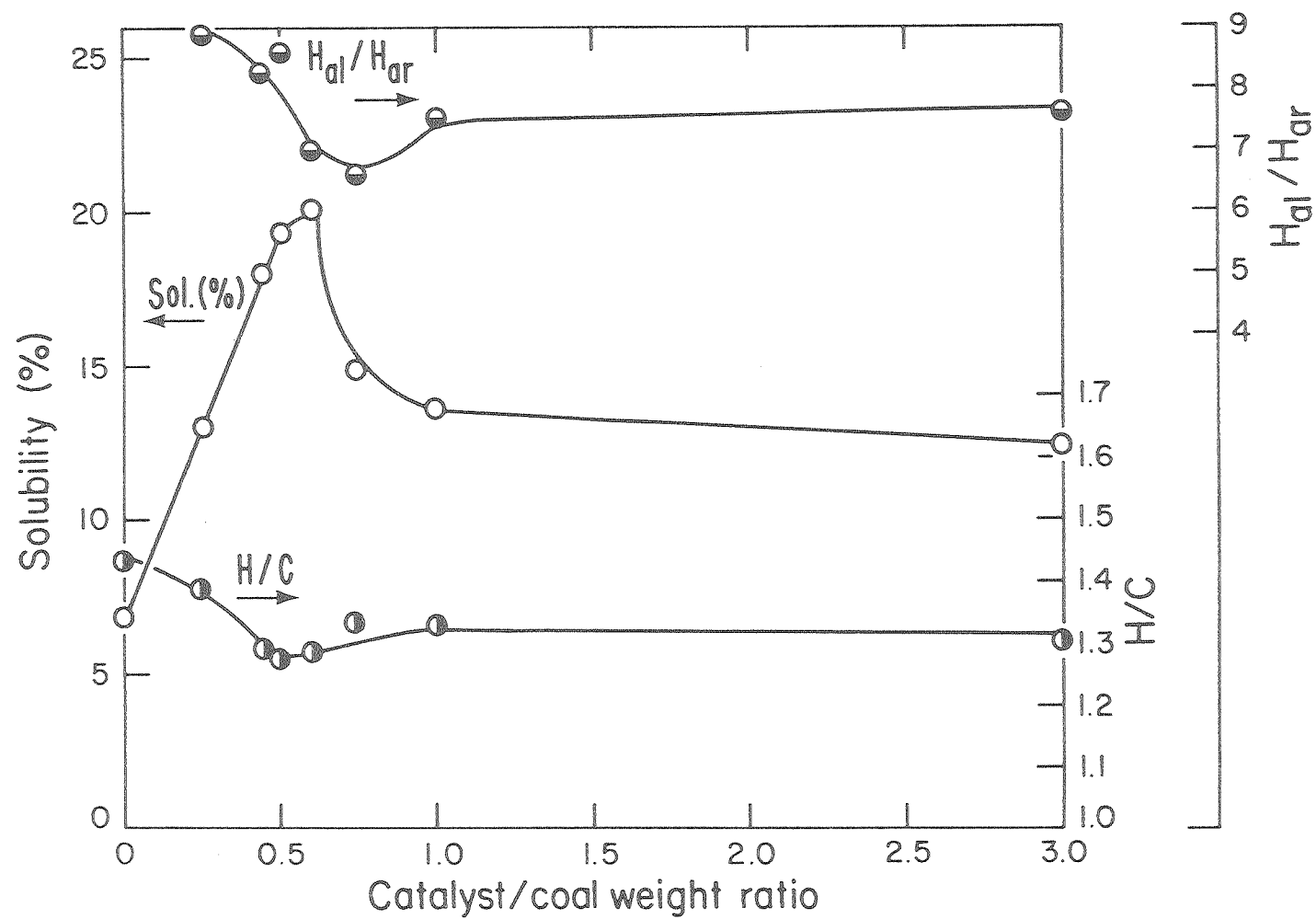
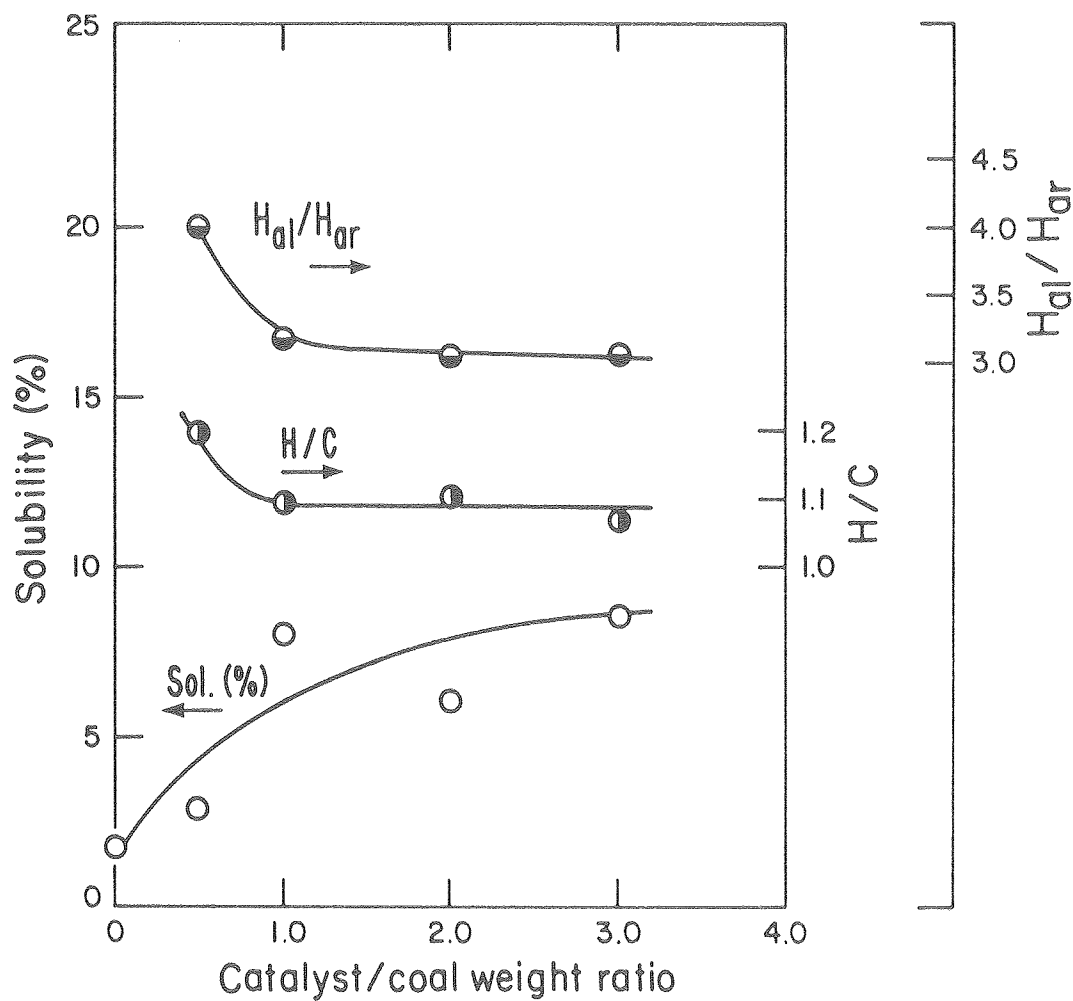


Figure 3-1. Effect of  $ZnCl_2$  Loading on Solubility, H/C ratio, and  $H_{al}/H_{ar}$  Ratio for Wyodak Coal.  
 $T = 300^\circ C$ ,  $P = 2000$  psig, Reaction time: 60 min. XBL 796-2023

causes the solubility to drop to 13.5% while any further increase in the ratio from 1.0 to 3.0 has little effect on the solubility. This trend suggests that two opposing types of reactions may be occurring. The first would involve breakage of bonds and subsequent hydrogenation of the fragments to produce a lower molecular weight substance. The second reaction would involve polymerization of the resulting fragments to produce tars. Excessive loading of zinc/chloride might physically inhibit the diffusion of the oil-like products into the solvent medium, with the result that the desired products might polymerize to form tar.

A similar series of runs were conducted using Illinois #6 coal. The data illustrated in Figure 3-2 and tabulated in 3-2, show that the cyclohexane solubility of the Illinois #6 is lower than that of the Wyodak coal, this probably due to the lower hydrogen content of the higher rank bituminous coal. The solubility obtained at the base conditions of 300°C and 2000 psig was 8.0% using zinc chloride, versus 1.8% without the catalyst. The amount of data obtained for Illinois #6 coal was limited, and conclusions on the effect of catalyst/coal weight ratio on the solubility of this coal cannot be made with certainty. The data do not reveal a peak at 0.6 catalyst to coal weight ratio as was present in the case with Wyodak. The percent solubility does begin to level off, however, at a catalyst to coal ratio of about 1.

The extracts obtained in each experiment were analyzed using  $^1\text{H}$ -NMR and elemental analysis. The  $^1\text{H}$ -NMR spectra at the base reaction conditions of 300°C and 2000 psig and



XBL 796-2024

Figure 3-2. Effect of  $ZnCl_2$  Loading on Solubility, H/C Ratio, and  $H_{al}/H_{ar}$  Ratio for Illinois #6 Coal.  
 $T = 300^\circ C$ ,  $P = 2000$  psig, Reaction Time = 60 min.



TABLE 3-2

Effect of Zinc Chloride Loading on Reaction Using Illinois #6 Coal

T = 300°C  
 P = 2000 psig  
 Time = 60 min

Coal = 5g  
 Catalyst = Zinc chloride  
 Solvent = 70 ml Cyclohexane

Run No.	Catalyst wt., g	Cat. Coal Ratio	Sol., % maf	Extract H/C	Analysis N/C	<sup>1</sup> H-NMR	
						H <sub>al</sub> /H <sub>ar</sub>	f <sub>a</sub>
29	0	0	1.8	-	-	-	-
70	2.5	0.5	2.9	1.19	0.0017	4.0	0.52
42	5.0	1.0	8.0	1.09	0.0018	3.3	0.58
73	10.0	2.0	6.0	1.10	0.0016	3.1	0.58
55	15.0	3.0	8.6	1.07	0.0010	3.1	0.59

catalyst to coal wt. ratio of 1 are presented for both Wyodak and Illinois #6 coals in Figure 3-3 and 3-4 respectively. The  $^1\text{H}$ -NMR data show that the extract from the Wyodak coal is less than the extract from the Illinois #6 coal. This is understandable, since Wyodak coal is less aromatic than Illinois #6 coal. In general, the  $^1\text{H}$ -NMR data for both coals reveal that the  $\text{H}_{\text{al}}/\text{H}_{\text{ar}}$  ratio decreases as the cyclohexane solubility increases. A possible explanation for this observation is that, as the degree of coal dissolution increases, more aromatic structural groups are released and enter into solution.

The elemental analyses follow a trend similar to that shown for the  $^1\text{H}$ -NMR data. In general, the extracts from the Wyodak coal showed higher H/C ratios compared to the extracts from Illinois #6 coal. In addition, within each data set, the H/C ratios decreased as solubility increased, the reason for this being the same as presented for the  $^1\text{H}$ -NMR data.

Nitrogen analyses of the extracts from Wyodak coal show that reaction in the presence of zinc chloride results in lower nitrogen content, most probably due to the formation of complexes between zinc chloride and compounds containing basic nitrogen. Tanner and Bell (18) have also reported lower nitrogen contents for SRC-I extracts treated in the presence of zinc chloride.

Experiments were also conducted with SRC-I. Since extensive work had been reported by Tanner and Bell (18) with this form of coal, a minimum amount of data was collected.

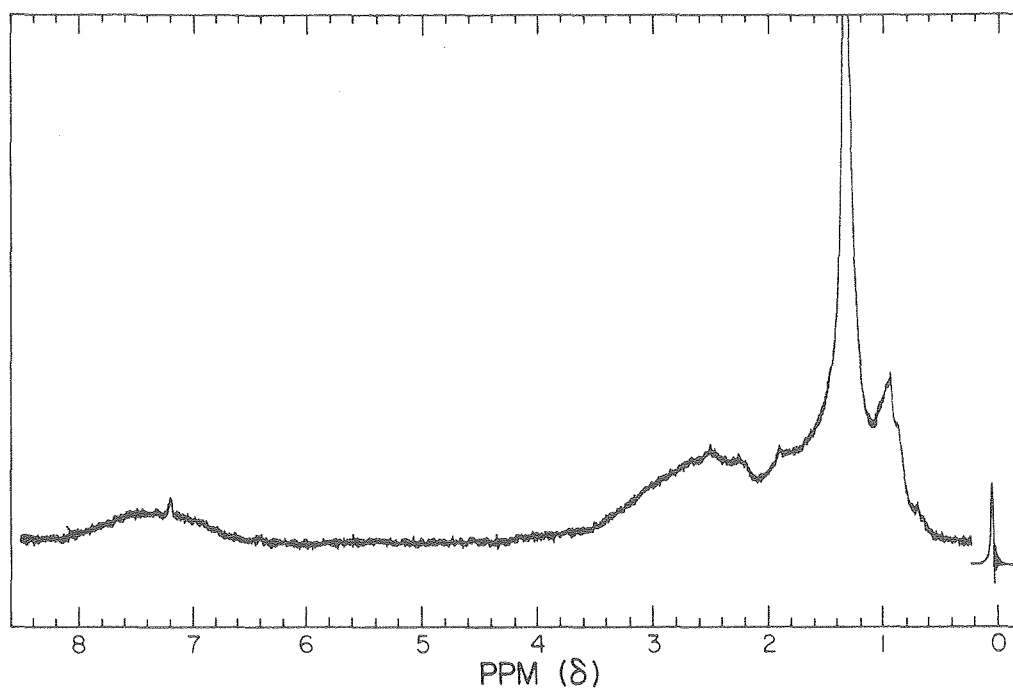


Figure 3-3.  $^1\text{H}$ -NMR Spectrum of Extract obtained from Wyodak Coal, reacted in Cyclohexane at 300°C and 2000 psig, using Zinc Chloride Catalyst.

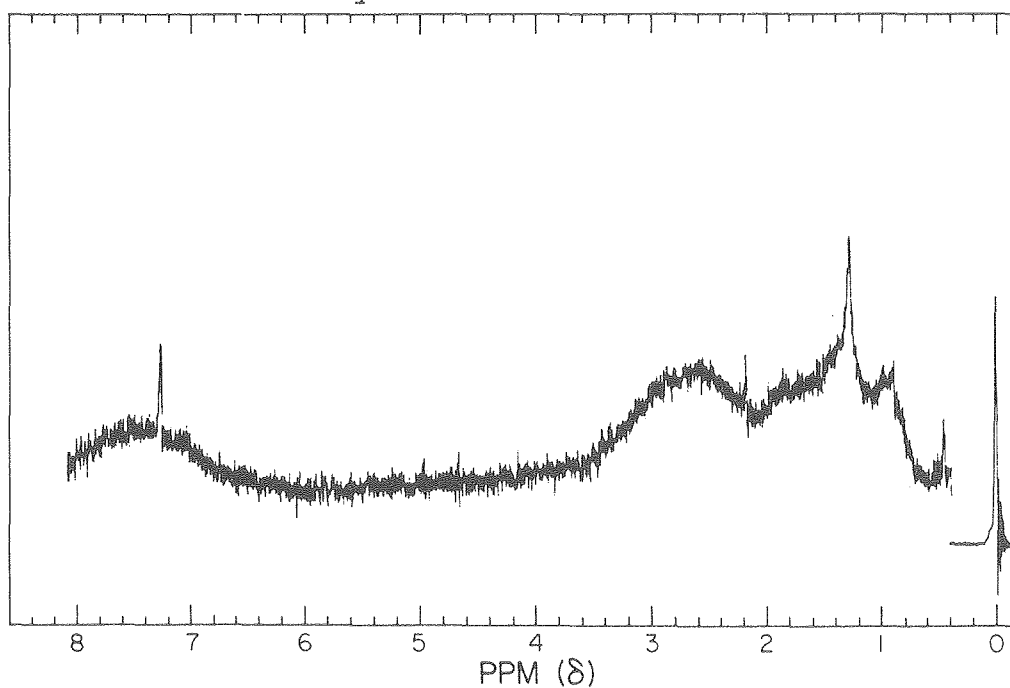


Figure 3-4.  $^1\text{H}$ -NMR Spectrum of Extract obtained from Illinois #6 Coal, reacted in Cyclohexane at 300°C and 2000 psig, using Zinc Chloride Catalyst. XBL 796-2014A

Table 3-3 shows that the cyclohexane solubility increases from 10% to 30% with the use of zinc chloride.

The effects of zinc chloride on SRC-II recycle slurry were also examined. Reactions were conducted with and without zinc chloride. The addition of zinc chloride catalyst had no beneficial effect and instead caused a reduction in cyclohexane solubility (see Table 3-3). As a consequence no further investigations were conducted using the SRC-II material.

The  $^1\text{H}$ -NMR spectra of the extracts obtained from both SRC-I and SRC-II recycled slurry are presented in Figure 3-5 and 3-6, respectively. The  $\text{H}_{\text{al}}/\text{H}_{\text{ar}}$  ratio of the SRC-I extract was comparable to the  $\text{H}_{\text{al}}/\text{H}_{\text{ar}}$  ratio for the Illinois #6 extract but much lower than the ratio for the Wyodak extract. Finally, the extract obtained from SRC-II recycle slurry was more aromatic than the extract obtained from any of the other three coals.

## 2. Reaction Time

The next set of experimental runs was performed to determine the effect of reaction time on cyclohexane solubility, using both Wyodak coal and SRC-I.

Reactions with Wyodak coal as illustrated in Table 3-4 and Figure 3-7 showed that the cyclohexane solubility increased up to about 120 minutes after which the solubility started to plateau out. In contrast, the  $\text{H}/\text{C}$  and  $\text{G}_{\text{al}}/\text{H}_{\text{ar}}$  ratios showed a downward trend indicating that even though the amount of oil-like products formed was higher with increasing reaction time, the products themselves were more aromatic and had a lower hydrogen to carbon

TABLE 3-3

Effect of Zinc Chloride Loading on Reaction using SRC-I and SRC-II

T = 300°C  
P = 2000 psig  
Time = 60 min

Coal = 5 g  
Catalyst = Zinc Chloride  
Solvent = 70 ml Cyclohexane

Run No.	Coal Type	Cat., g	Sol., % maf	Extract $H_{al}/H_{ar}$
32	SRC I	0	10.6	1.6
5	SRC I	5.0	30.0	3.3
33	SRC II	0	49.9	1.4
34	SRC II	5.0	43.6	1.6

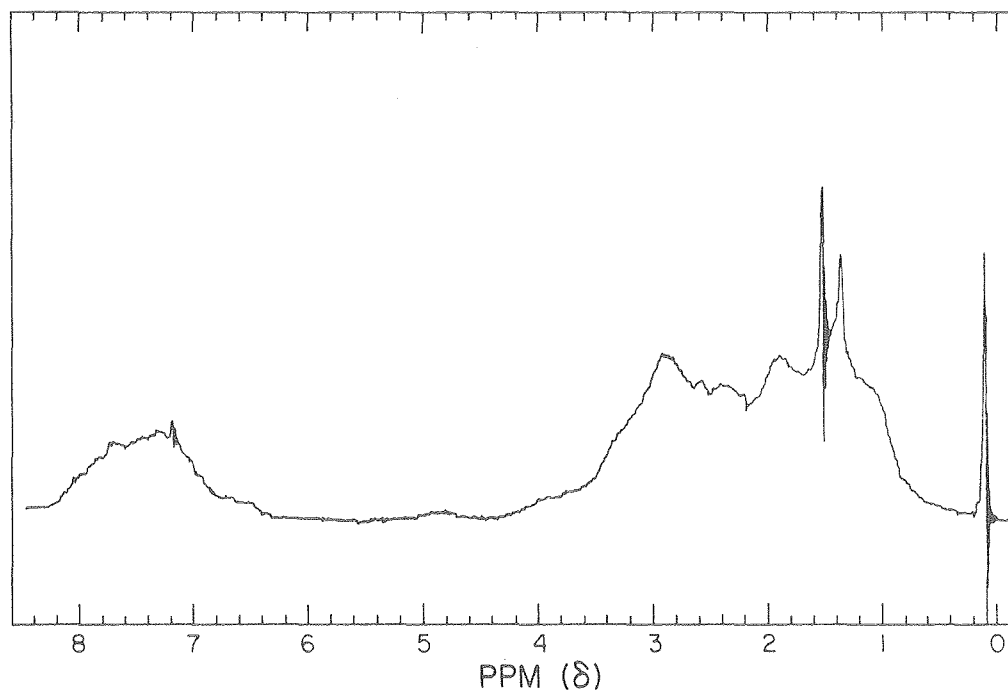
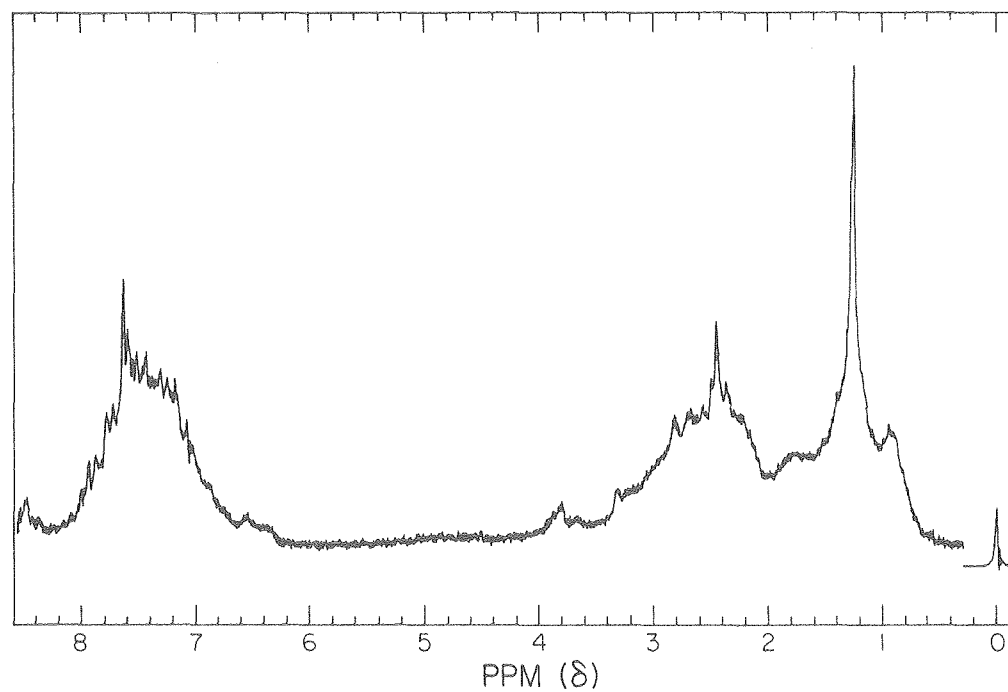


Figure 3-5. <sup>1</sup>H-NMR Spectrum of Extract obtained from SRC-I, reacted in Cyclohexane at 300°C and 2000 psig, using Zinc Chloride Catalyst.



XBL 796-2016A

Figure 3-6. <sup>1</sup>H-NMR Spectrum of Extract obtained from SRC-II Recycled Slurry, reacted in Cyclohexane at 300°C and 2000 psig, using Zinc Chloride Catalyst.

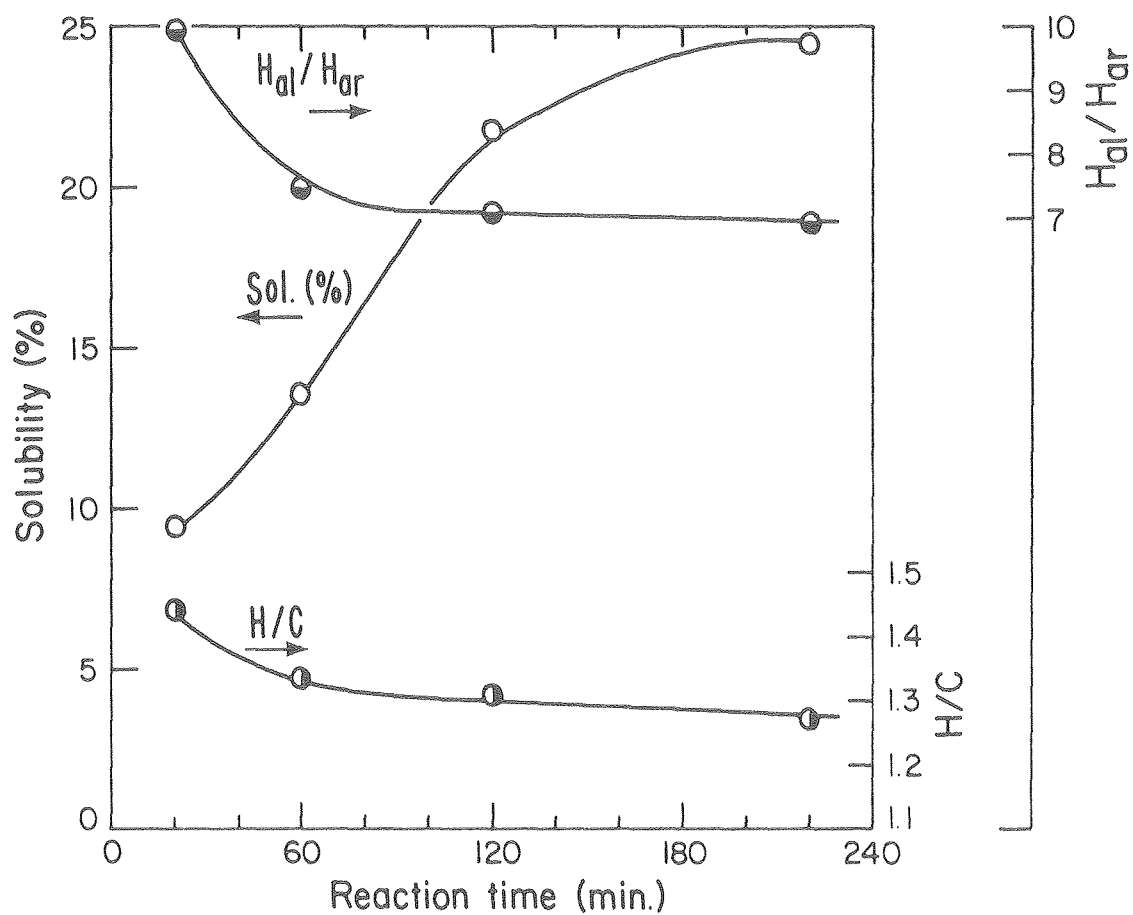
TABLE 3-4

Effect of Run Time on Reaction using Wyodak Coal

T = 300°C  
P = 200 psig

Coal = 5 g Wyodak  
Catalyst = 5 g Zinc Chloride  
Solvent = 70 ml Cyclohexane

Run No.	Reaction Time, min.	Sol., % maf	Extract Analysis		<sup>1</sup> H-NMR Data	
			H/C	O/C	H <sub>al</sub> /H <sub>ar</sub>	f <sub>a</sub>
62	20	9.4	1.43	0.0715	9.9	0.35
25	60	13.5	1.33	0.049	7.5	0.41
63	120	21.9	1.31	0.051	7.1	0.43
74	220	24.7	1.27	0.042	6.9	0.45



XBL 796-2025

Figure 3-7. Effect of Reaction Time on Solubility,  $H/C$  Ratio, and  $H_{al}/H_{ar}$  Ratio for Wyodak Coal.  
 $T = 300^{\circ}\text{C}$ ,  $P = 2000$  psig, Cat./Coal weight ratio = 1.0.



content. In addition, the oxygen content of the extract decreased with increasing reaction time, possibly indicating cleavage of ether bonds.

The second set of experimental runs to determine the effect of reaction time was conducted with SRC-I. Table 3-5 and Figure 3-8 summarize the data. These results indicate that extraction of SRC-I into cyclohexane was complete after about 60 minutes, and that the  $H_{al}/H_{ar}$  ratio increases with longer reaction time.

Comparing the reaction time data for Wyodak coal versus SRC-I, one can observe that the  $H_{al}/H_{ar}$  data follow different paths. One possible reason for this could be that different types of bonds are being cleaved in the two substrates. In the case of SRC-I, cleavage of ether linkages is probably minimal, since the solvent refining process itself has already accomplished that task. For Wyodak coal cleavage of ether bonds is possibly a predominant process, as suggested by the lowering of the oxygen content. Another possible reason for the differences in the  $H_{al}/H_{ar}$  ratio trends for SRC-I and Wyodak coal is that different sources of hydrogen are used to hydrogenate fragments formed during depolymerization. In the case of the less aromatic Wyodak coal, a greater fraction of the necessary hydrogen may come from hydroaromatic portions of the coal structure.

### 3. Temperature and Pressure

The effect of reaction temperature and reaction pressure on the cyclohexane solubility of Wyodak coal and the

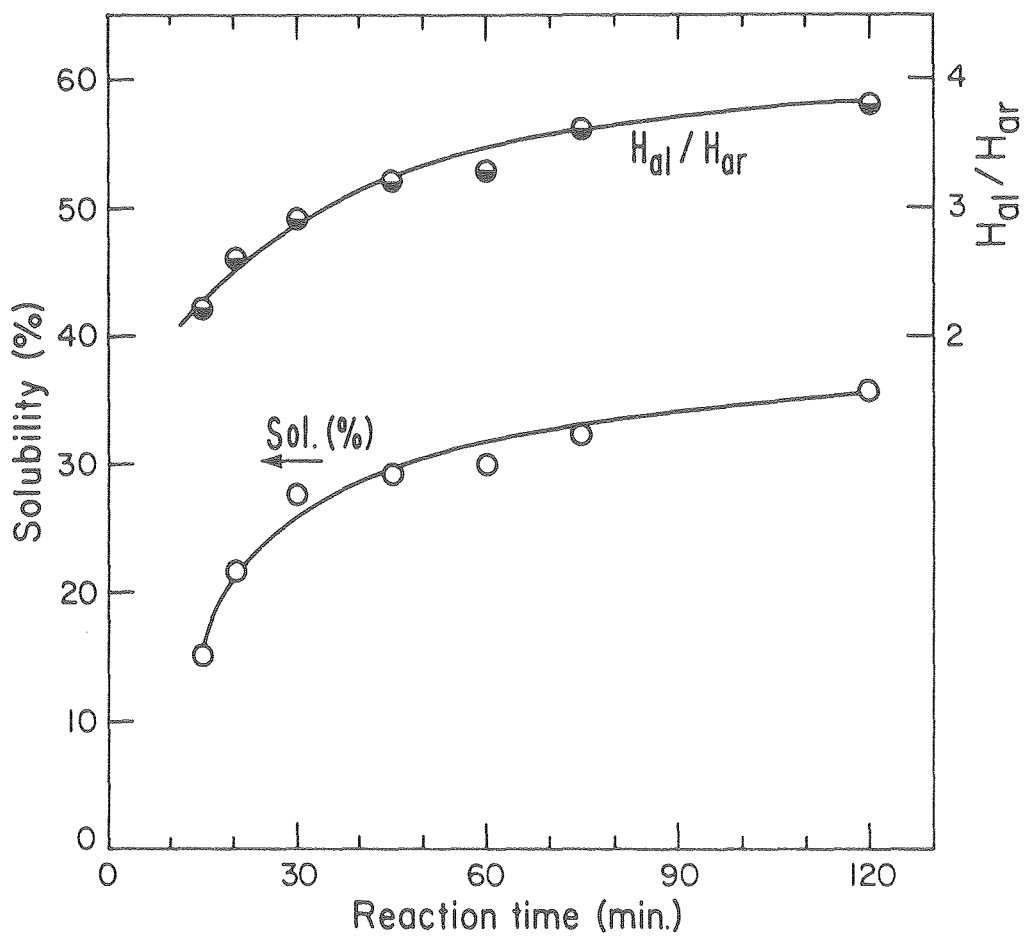
TABLE 3-5

Effect of Run Time on Reaction Using SRC-I

T = 300°C  
P = 2000 psig

Coal = 5 g  
Catalyst = 5 g Zinc Chloride  
Solvent = 70 ml Cyclohexane

Run No.	Reaction Time, min.	Sol., % maf	Extract $H_{al}/H_{ar}$
8	15	15.0	2.2
11	20	21.6	2.6
6	30	27.5	2.9
10	45	29.9	3.2
5	60	30.0	3.3
9	75	32.0	3.6
7	120	35.3	3.8



XBL 796-2026

Figure 3-8. Effect of Reaction Time on Solubility and  $H_{al}/H_{ar}$  Ratio for SRC-I.  
 $T = 300^{\circ}\text{C}$ ,  $P = 2000$  psig, Cat./Coal weight ratio = 1.0.

characteristics of the soluble material was investigated in two sets of runs.

Table 3-6 and Figure 3-9 present the temperature dependent data with and without the use of zinc chloride catalyst. The solubility in both cases increases linearly between 250°C and 400°C the maximum range of reaction temperatures studied in this investigation. The data also show that the presence of zinc chloride causes the solubility of the coal to roughly double. In addition, it is seen that the soluble material obtained with the use of zinc chloride at a fixed temperature is more aromatic and has lower H/C and N/C ratios than the soluble material obtained in the absence of the catalyst.

The effects of increasing reaction temperature on the H/C ratio, the  $H_{al}/H_{ar}$  ratio, and the oxygen content are similar to those observed with increasing reaction time at a fixed temperature. All three characteristics decrease with higher temperature. Figure 3-10 and 3-11 present  $^1H$ -NMR spectra of the extracts obtained at reaction temperatures of 250°C and 400°C, respectively.

The effects of hydrogen pressure on the solubility and characteristics of the soluble products are not as great as those of temperature. As the reaction pressure is raised from 680 psig to 3000 psig the cyclohexane solubility increases from 10.6% to 17.3% as shown in Table 3-7 and Figure 3-12. However, Run #66 shows that the hydrogen does have a role in the reaction, since the cyclohexane solubility dropped to only 5.4% when the reaction was conducted under

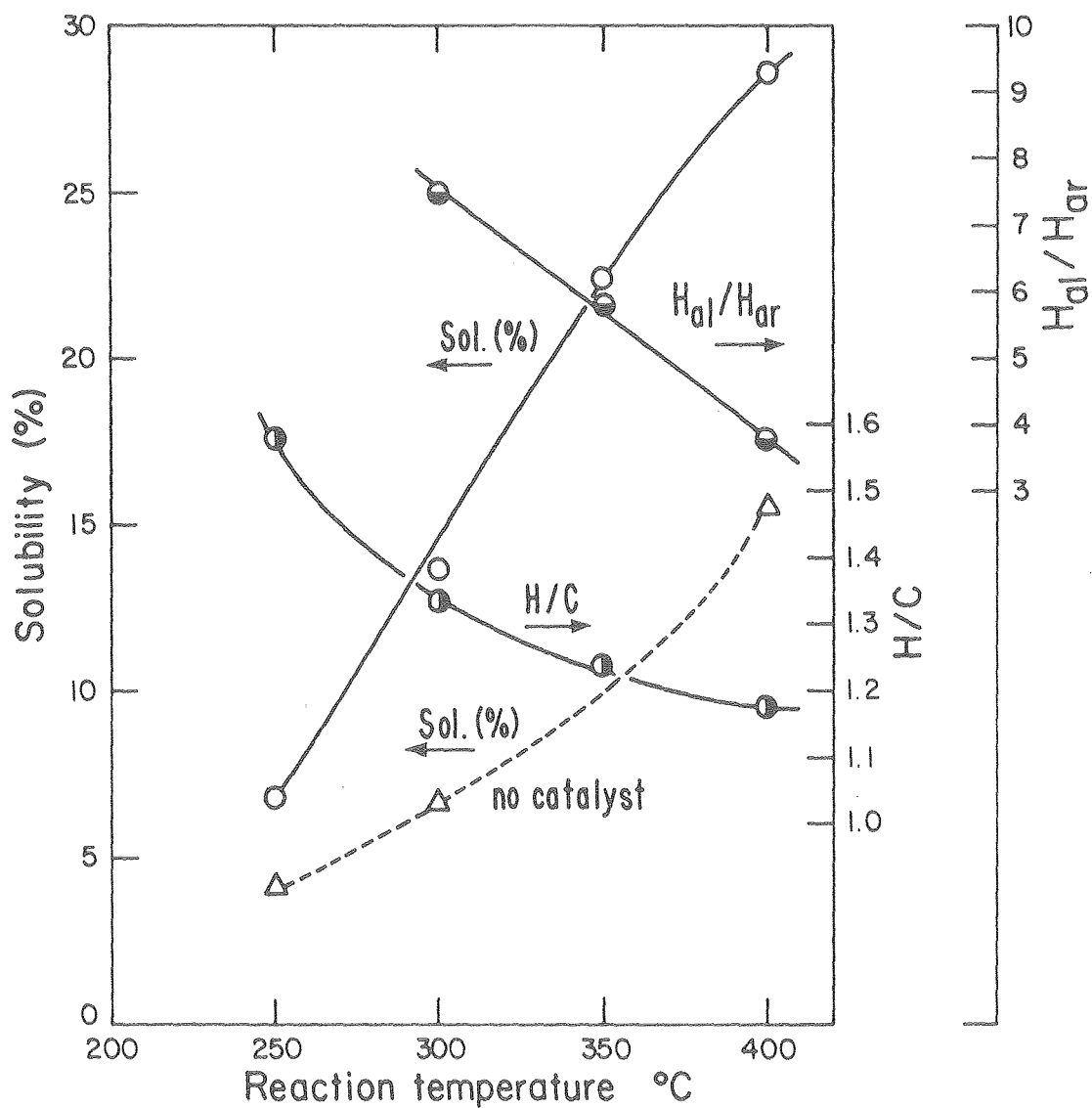
TABLE 3-6

Effect of Temperature on Reaction Using Wyodak Coal

P = 2000 psig  
Time = 60 min

Coal = 5 g  
Catalyst = Zinc Chloride  
Solvent = 70 ml Cyclohexane

Run No.	Cat., g	Temp., °C	Sol., % maf	Extract Analysis			<sup>1</sup> H-NMR H <sub>al</sub> /H <sub>ar</sub>	f <sub>a</sub>
				H/C	O/C	N/C		
64	5.0	250	6.8	1.58	0.092	0.0013	>10	-
25	5.0	300	13.5	1.33	0.049	0.0015	7.5	0.41
65	5.0	350	22.5	1.23	0.038	0.0015	5.9	0.47
68	5.0	400	28.4	1.17	0.020	0.0016	3.7	0.53
75	0.0	250	4.1	1.67	0.081	0.0015	>10	-
69	0.0	300	6.9	1.44	0.056	0.0053	>10	-
76	0.0	400	15.5	1.49	0.041	0.0060	6.9	0.39



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Figure 3-9. Effect of Reaction Temperature on Solubility, H/C Ratio, and  $H_{al}/H_{ar}$  for Wyodak Coal.  
 P = 2000 psig, Reaction Time = 60 min.,  
 Cat/Coal weight ratio = 1.0.

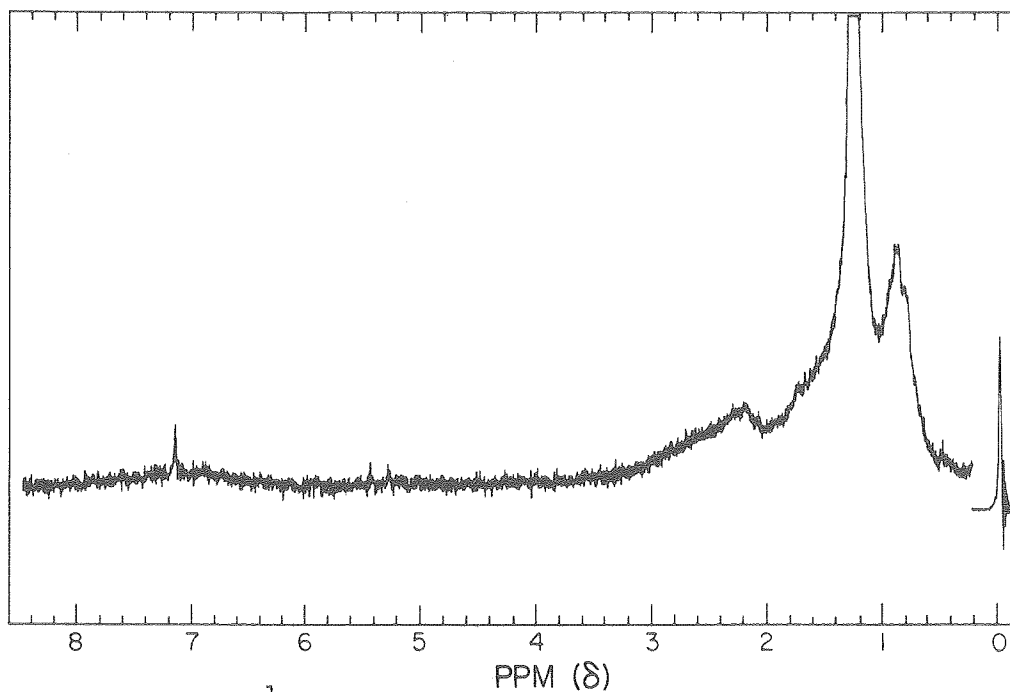
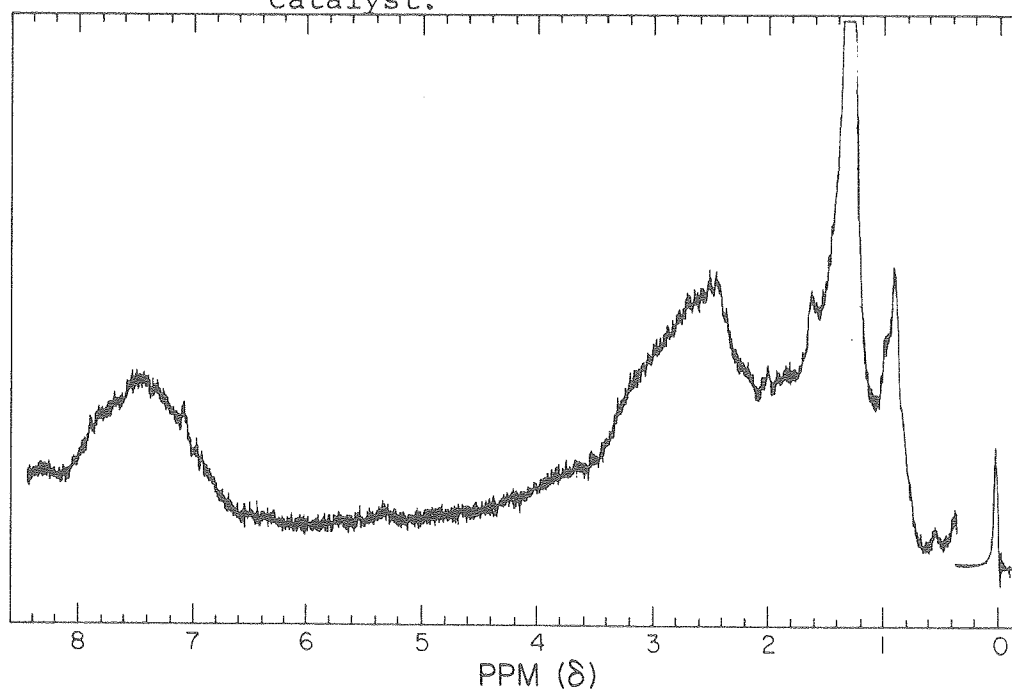


Figure 3-10.  $^1\text{H}$ -NMR Spectrum of Extract obtained from Wyodak Coal, reacted in Cyclohexane at 250°C and 2000 psig, using Zinc Chloride Catalyst.



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Figure 3-11.  $^1\text{H}$ -NMR Spectrum of Extract obtained from Wyodak Coal, reacted in Cyclohexane at 400°C and 2000 psig, using Zinc chloride Catalyst.

TABLE 3-7

Effect of Hydrogen Pressure on Reaction Using Wyodak Coal

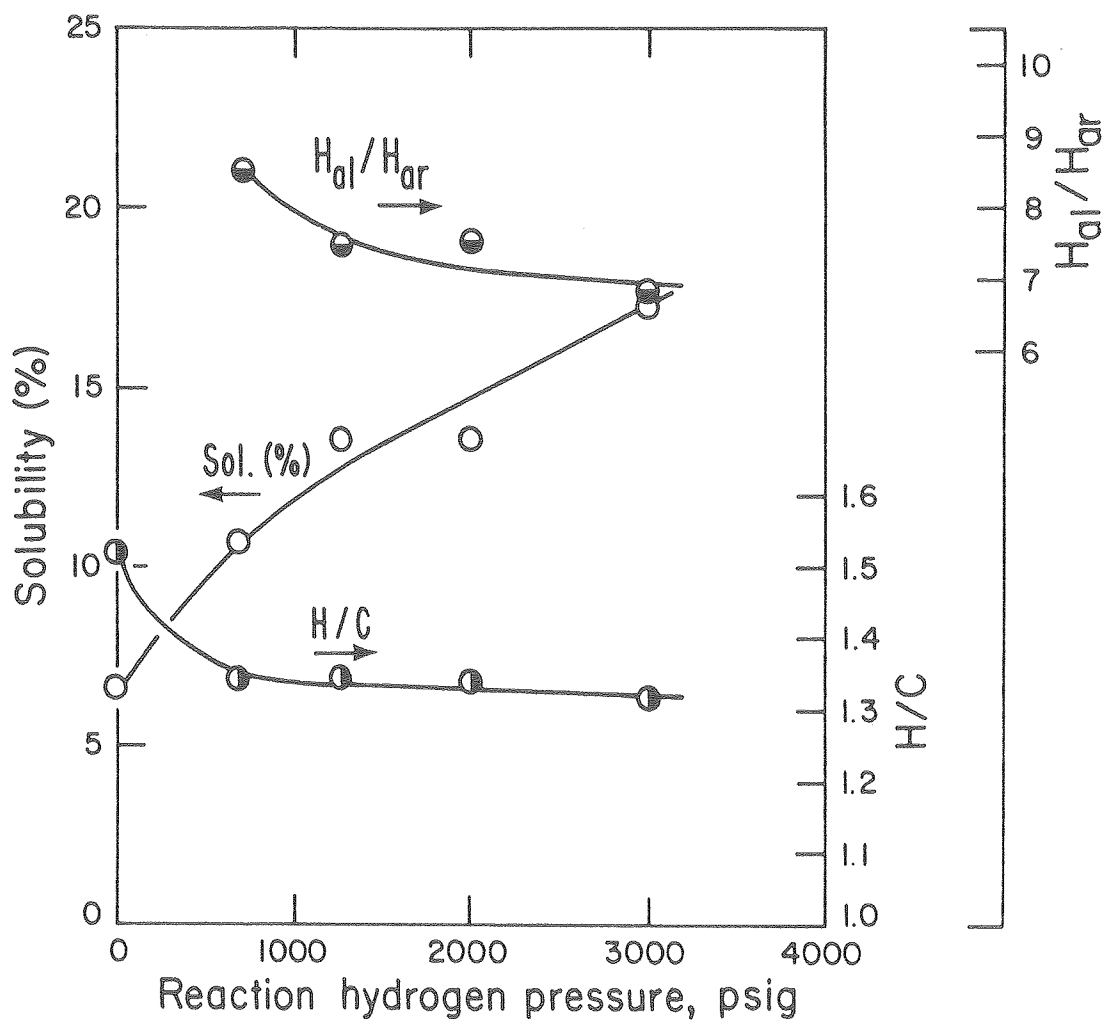
T = 300°C  
 Time = 60 min.

Coal = 5 g  
 Catalyst = 5 g Zinc Chloride  
 Solvent = 70 ml Cyclohexane

Run No.	Hydrogen Pressure, psi	Sol., % maf	Extract Analysis		<sup>1</sup> H-NMR Data	
			H/C	O/C	H <sub>al</sub> /H <sub>ar</sub>	f <sub>a</sub>
66	0 <sup>a</sup>	6.3	1.52	0.058	10	-
61	680	10.6	1.34	0.065	8.5	0.40
60	1230	13.5	1.34	0.067	7.5	0.41
25	2000	13.5	1.33	0.049	7.5	0.41
67	3000	17.3	1.32	0.049	6.8	0.42

<sup>a</sup> Nitrogen pressure of 2000 psig





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Figure 3-12. Effect of Hydrogen Pressure on Solubility,  $H/C$  Ratio, and  $H_{al}/H_{ar}$  for Wyodak Coal.  
 $T = 300^{\circ}\text{C}$ , Reaction time = 60 min.,  
 Cat/Coal weight ratio = 1.0.

nitrogen at 2000 psig instead of hydrogen as was the case with the other runs.

The effects of increasing reaction pressure on the H/C ratio and the  $H_{al}/H_{ar}$  ratio is similar to those noted with increasing temperature at a fixed pressure. Both the H/C ratio and the  $H_{al}/H_{ar}$  decrease as the solubility increases; however, both characteristics are nearly constant at pressures in excess of 1000 psig.

#### B. Effect of Co-catalysts and Additives

The next phase of the experimental research was aimed at examining the use of co-catalysts and additives together with zinc chloride with the aim of increasing the yield of oil-like products.

##### 1. Co-catalysts

The following materials were investigated as co-catalysts to be used with zinc chloride: zinc, nickel, nickel sulfide, and aluminum chloride.

##### a. Zinc Metal

Work with coal model compounds by Mobley and Bell (23) had indicated that a zinc chloride-zinc metal mixture was more effective than zinc chloride alone in converting bibenzyl ether to toluene. Since the cleavage of ether linkages is a potentially significant step in coal liquefaction, the use of a zinc-zinc chloride system was examined.

The first substrate investigated was Illinois #6 coal. The results as indicated in Table 3-8 show that the cyclohexane solubility dropped relative to that obtained when only

TABLE 3-8

## Effect of Zinc Metal as a Co-catalyst

T = 300°C                      Coal = 5 mg  
 P = 2000 psig                Solvent = 70 ml Cyclohexane  
 Time = 60 min.

Run No.	Substrate Type	ZnCl <sub>2</sub> g	Zn Metal, g	Sol., % maf	Extract Analysis H/C	<sup>1</sup> H-NMR Data H <sub>al</sub> /H <sub>ar</sub>	f <sub>a</sub>
25	Wyodak	5.0	0	13.5	1.33	7.5	0.41
26	Wyodak	2.5	1.2	13.7	1.39	10.2	0.37
42	Illin. #6	5.0	0	8.0	1.09	3.3	0.58
30	Illin. #6	2.5	1.2	2.3	-	4.8	-
53	SRC-I	5.0	0	30.0	-	3.3	-
14	SRC-I	3.7	0.6	19.5	-	2.4	-
13	SRC-I	2.5	1.2	17.0	-	2.1	-

zinc chloride was used. The results could be explained on the basis that the beneficial role of the zinc as a hydrogenating agent was not fully utilized, and the drop in solubility was a result of the decreased zinc chloride loading since the total number of moles of zinc was kept constant in all cases. Similar results were observed for SRC-I.

Experiments with Wyodak coal, however, showed that the same mixture of zinc chloride-zinc did not cause a reduction in the cyclohexane solubility. This could be explained on the basis that the optimum zinc chloride loading as determined from the catalyst loading-rate data was approximately 0.6 catalyst to coal by weight. Since this optimum ratio was approached with the proportional decrease in the zinc chloride as zinc metal was added, the negative effect of zinc was not apparent.

Overall, for both the Wyodak and Illinois #6 coals, the  $H/C$  and  $H_{al}/H_{ar}$  ratios showed a slight increase indicating that the zinc was possibly serving as a hydrogenating catalyst, but one of very low activity.

b. Nickel and Nickel Sulfide

Work by Mobley and Bell (23) had also shown a remarkable increase in the conversion of bibenzylether to toluene when using nickel and nickel sulfide as hydrogenating agents with zinc chloride. Correspondingly, experiments were conducted using these co-catalysts in combination with zinc chloride. As illustrated in Table 3-9, the nickel zinc chloride catalyst mixture caused the cyclohexane solubility of Wyodak

TABLE 3-9

Effect of Ni and NiS as Co-catalysts

T = 300°C  
 P = 2000 psig  
 Time = 60 min.

Coal = 5g  
 Solvent = 70 ml Cyclohexane

Run No.	Substrate Type	ZnCl <sub>2</sub> g	Ni, g	NiS, g	Sol., % maf	Extract Analysis H/C	<sup>1</sup> H-NMR Data H <sub>al</sub> /H <sub>ar</sub>	f <sub>a</sub>
25	Wyodak	5.	0	0	13.5	1.33	7.5	0.41
49	Wyodak	2.5	2.1	0	19.9	1.28	7.0	0.44
50	Wyodak	2.5	0	1.7	12.2	1.50	10.1	0.32
53	Wyodak	0	0	3.4	6.0	-	-	-
42	Illin.#6	5.	0	0	8.0	1.09	3.3	0.58
48	Illin.#6	2.5	2.1	0	12.6	1.12	3.6	0.56

coal to rise up to 19.9% showing that nickel had a higher activity than zinc. For Wyodak coal, the optimum catalyst loading with only zinc chloride was previously determined to be 0.6 catalyst/coal by weight, in which case 20.0% of the coal was soluble in cyclohexane. This optimum loading was approached with the proportional decrease in the zinc chloride as nickel metal was added. Therefore, the proportional effect of nickel is not conclusive with the Wyodak data. However, an increase in activity was definitely observed using Illinois #6 coal, in which case the solubility increased from 8.0% with zinc chloride alone to 12.6% with the nickel-zinc chloride catalyst mixture.

Because of the presence of sulfur in the coal, some of the nickel would conceivably be converted to nickel sulfide; thus, reactions were then conducted using a nickel sulfide-zinc chloride catalyst mixture. This catalyst mixture did not increase the cyclohexane solubility, possibly reflecting poor catalyst-coal contacting.

#### c. Aluminum Chloride-Zinc Chloride

Aluminum chloride is a strong Lewis acid in comparison to zinc chloride. However, aluminum chloride used by itself is a less effective catalyst for producing liquid products, and instead accelerates the formation of char and gas. However, it was of interest to see whether a zinc chloride-aluminum chloride mixture would be more effective than zinc chloride alone, since the chlorides could form a complex

exhibiting unique catalytic properties. Experimental results taken with SRC I (see Table 3-10) indicated this apparently did not occur; both the cyclohexane solubility and the  $H_{al}/H_{ar}$ /ratio dropped with the addition of even 10 mole % of aluminum chloride.

#### 1. Alcohol Additives

In previous studies (18, 36), it had been established that alcohols will alkylate the coal structure and thereby increase the cyclohexane solubility. Experiments were conducted to indentify the effect of different alcohols in the presence of zinc chloride on all three coals used in this study.

Methanol and isopropanol were used as additives with Wyodak and Illinois #6 coals. These reaction are summarized in Table 3-11. The  $^1H$ -NMR spectra of the extract from both Wyodak and Illinois #6 coals reacted in the presence of isopropanol are given in Figures 3-13 and 3-14, respectively. For both substrates the use of methanol and isopropanol as alkylating agents did cause a considerable increase in the amounts of material soluble in cyclohexane. This increase could be attributed either to changes in the actual coal structure or merely to incorporation of the alcohol into the coal structure. Overall, isopropanol caused a more dramatic increase in the solubility than methanol.

The alcohols used as additives with SRC I were methanol, ethanol, isopropanol, and t-butanol (see Table 3-12). All showed signs of alkylation, and all except t-butanol showed

TABLE 3-10

Effect of  $\text{AlCl}_3$  as a Co-catalyst

T = 300°C  
P = 2000 psig  
Time = 60 min.

Coal = 5g SRC-I  
Solvent = 70 ml Cyclohexane

Run No.	$\text{ZnCl}_2$ g	$\text{AlCl}_3$ g	Sol., % maf	$\text{H}_{\text{al}}/\text{H}_{\text{ar}}$ Ratio
32	0	0	10.6	1.6
5	5.0	0	30.0	3.3
15	4.5	0.5	19.4	2.1
16	4.0	1.0	13.3	1.6



TABLE 3-11

Effect of Alcohols on Reactions Using Wyodak and Illinois #6 Coals

T = 300°C  
 P = 2000 psig  
 Time = 60 min

Coal = 5g  
 Catalyst = 5g  
 Solvent = 70 ml Cyclohexane

Run No.	Coal Type	Additive Type	Additive Weight,g	Sol., % maf	Extract H/C	Analysis O/C	<sup>1</sup> H-NMR H <sub>al</sub> /H <sub>ar</sub>	Data f <sub>a</sub>
25	Wyodak	None	0	13.5	1.33	0.049	7.5	0.41
27	Wyodak	Isoprop.	5.	46.7	1.28	0.123	7.8	0.43
42	Illin.#6	None	0.	8.0	1.09	0.062	3.3	0.58
31	Illin.#6	Isoprop.	5.	36.4	1.19	0.084	5.8	0.49
43	Illin.#6	Methanol	1.2	16.7	1.14	0.076	5.4	0.52
71	Illin.#6	Methanol	5.	19.8	1.17	0.083	6.9	0.49

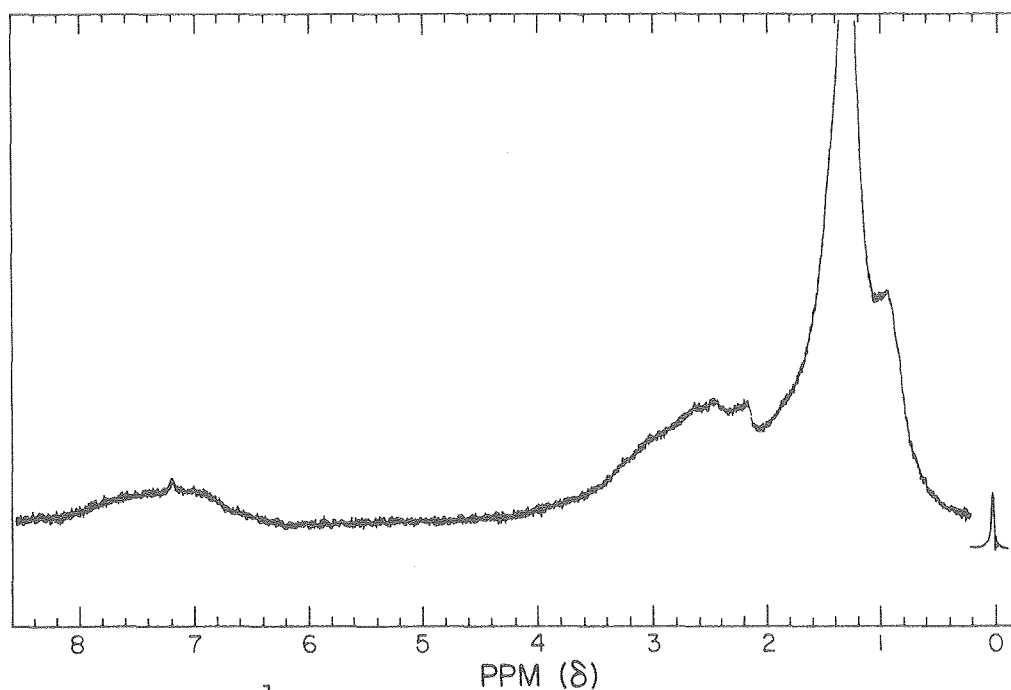
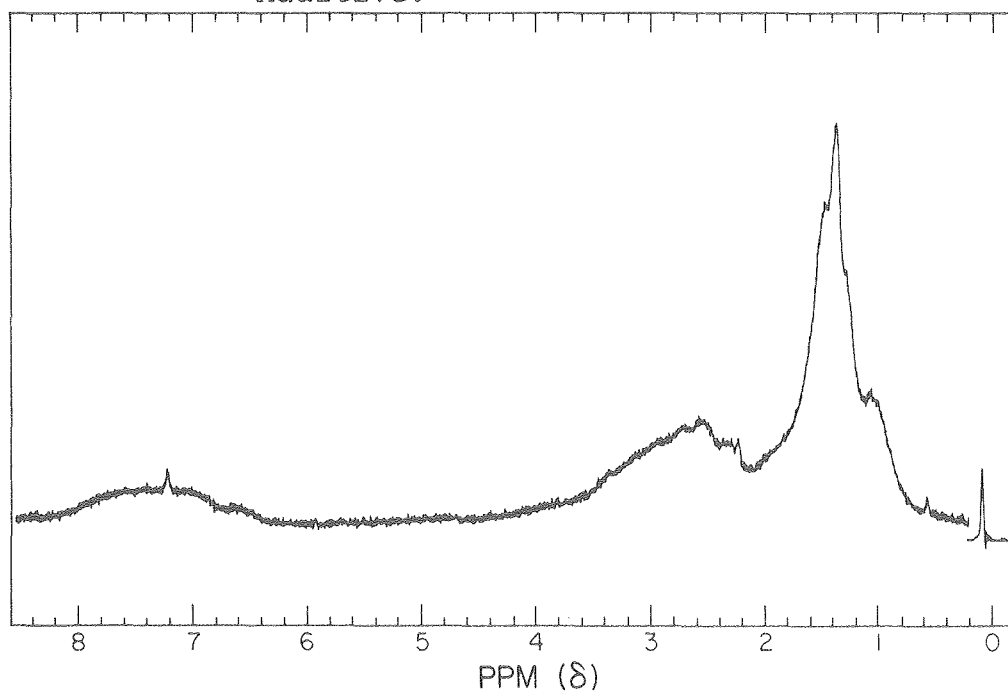


Figure 3-13.  $^1\text{H}$ -NMR Spectrum of Extract obtained from Wyodak Coal, reacted in Cyclohexane at 300°C and 2000 psig, using Zinc Chloride Catalyst and Isopropanol Additive.



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Figure 3-14.  $^1\text{H}$ -NMR Spectrum of Extract obtained from Illinois #6 Coal, reacted in Cyclohexane at 300°C and 2000 psig, using Zinc Chloride Catalyst and Isopropanol Additive.

TABLE 3-12

## Effect of Alcohols on Reactions Using SRC I

T = 300°C  
P = 2000 psig  
Time = 60 min.

Coal = 5g  
Catalyst = 5g Zinc Chloride  
Solvent = 70 ml Cyclohexane

Run No.	Additive Type	Additive Weight, g	Sol., % maf	<sup>1</sup> H-NMR Data H <sub>al</sub> /H <sub>ar</sub>
5	None	0	30.0	3.3
18	Methanol	5	41.5	4.2
19	Ethanol	5	52.0	5.3
20	Isopropanol	5	52.4	5.4
21	t-butanol	5	30.3	2.8

increased cyclohexane solubility of the products. Isopropanol and ethanol were found to show the greatest effect on the solubility, while t-butanol showed appreciably less activity possibly because the t-butanol decomposed to gases such as isobutene.

In general, as mentioned earlier, the large increase in cyclohexane solubility obtained when using alcohols such as isopropanol could be due to the enhanced hydrogen donor ability of this solvent. However, alkylation may also be a strong factor as illustrated by Tanner and Bell (18), who reported that up to 12% of the isopropanol additive alkylated the soluble products of SRC-I dissolved in cyclohexane. Where alcohol additives were used, the resulting extracts were hard and brittle. By contrast, the extracts obtained in the absence of alcohols had the appearance of a viscous oil.

### C. Effect of Changes in Reaction Method

#### 1. Impregnation of Zinc Chloride from Methanol Solution

Two improved coal-catalyst contacting techniques were investigated in order to increase the conversion of coal to oil like products.

The first method involved impregnation of coal with zinc chloride from a methanol solution of the catalyst. The melt and the moisture free coal were thoroughly mixed with each other. Thereafter, all the methanol was evaporated off at 105°C and the resulting impregnated coal was reacted

at the base conditions of 300°C and 2000 psig with a catalyst to coal ratio of 1. Results for both Wyodak and Illinois #6 coals, as tabulated in Table 3-13, show that no improvements were observed in either case using the impregnation technique. This indicates that the zinc chloride-coal contact achieved in the absence of impregnation was adequate and that contact between the coal and the catalyst does not limit the rate of coal liquefaction.

Another technique used was the methanol wash impregnation technique. In this method the coal was used without pre-drying as was the case with the other experiments. The wet coal was first washed with methanol and then mixed with a methanol-zinc chloride melt, with the aim of driving the zinc chloride into the pore structure of the coal by concentration difference. These experiments were conducted with Illinois #6 coal, and the results are given in Table 3-14. Results show no improvement in the cyclohexane solubility versus mixing methanol directly with the rest of the reactants.

## 2. Effect of Solvent to Coal Ratio

Several experiments were conducted to study the effect of varying the solvent to coal ratio. As illustrated in Table 3-15, changing the solvent/coal ratio between 7 and 21 ml/g had no effect on the cyclohexane solubility. This data indicates that the solvent does not reach saturation, and that separation of the desired oil-like products from

TABLE 3-13

Effect of Methanol Impregnation on Reactions  
Using Wyodak and Illinois #6 Coal

T = 300°C  
P = 2000 psig  
Time = 60 min.

Coal = 5g  
Catalyst = 5g Zinc Chloride  
Solvent = 70 ml Cyclohexane

Run No.	Coal Type	Impreg- nation	Sol., % maf	Extract Analysis H/C	<sup>1</sup> H-NMR H <sub>al</sub> /H <sub>ar</sub>	Data f <sub>a</sub>
25	Wyodak	No	13.4	1.33	7.5	0.41
44	Wyodak	Yes	14.7	1.35	8.6	0.40
42	Illinois #6	No	8.0	1.09	3.3	0.58
41	Illinois #6	Yes	7.8	1.10	3.4	0.58

TABLE 3.14

Effect of Methanol Wash and Impregnation on Reaction using Illinois #6 Coal

T = 300°C  
 P = 2000 psig  
 Time = 60 min.

Coal = 5g  
 Catalyst = 5g Zinc Chloride  
 Solvent = 70 ml Cyclohexane

Run No.	Impreg- nation	Additive	Additive Weight, g	Sol., % maf	Extract Analysis H/C	<sup>1</sup> H-NMR Data	
						H <sub>al</sub> /H <sub>ar</sub>	f <sub>a</sub>
42	No	None	0	8.0	1.09	3.3	0.58
71	No	Methanol	5	19.8	1.17	6.9	0.49
72	Yes	Methanol	5	14.2	1.17	5.9	0.50

TABLE 3.15

Effect of Solvent-Coal Ratio on Reactions using Wyodak Coal

T = 300°C  
 P = 2000 psig  
 Time = 60 min.

Coal = Wyodak  
 Catalyst = Zinc Chloride  
 Solvent = Cyclohexane

Run No.	Coal wt. <sup>a</sup> , g	Solvent, ml	Sol./Coal Ratio	Sol., % maf	Extract Analysis H/C	<sup>1</sup> H-NMR H <sub>al</sub> /H <sub>ar</sub>	Data f <sub>a</sub>
46	5	105	21	13.5	1.40	7.4	0.38
25	5	70	14	13.5	1.33	7.5	0.41
47	10	70	7	13.5	1.38	7.3	0.39
45	5	35	7	9.0	1.35	10.0	0.39



the solvent phase was minimal during the cooling cycle. Reducing the absolute amount of solvent to 35 ml caused a decrease in the cyclohexane solubility, possibly due to poor agitation or inadequate contacting of the coal and the solvent.

### 3. Effect of Using Benzene as the Extracting Solvent

In order to see the effect of changing the extracting solvent, experiments were conducted in benzene. Table 3-16 compares the solubility and other characteristics of the extracts obtained using benzene and cyclohexane. As expected, the solubilities were somewhat higher in benzene since this solvent extracts not only the oil like products as is the case with cyclohexane but also the asphaltene content of the products. However, benzene has a tendency to alkylate and cap of the coal fragments in the presence of zinc chloride (24). This results in incorporation of the solvent onto the soluble products. Therefore, the solubility data may not give an accurate indication of the amount of the coal soluble in benzene.

Table 3-16 also shows that the benzene extracts were more aromatic and exhibited lower H/C ratios and higher N/C ratios than the cyclohexane extracts. The  $^1\text{H}$ -NMR spectra using benzene solvent for both Wyodak and Illinois #6 coals are given in Figures 3-15 and 3-16, respectively.

TABLE 3.16

Effect of Solvent on Reactions Using Wyodak and Illinois #6 Coals

T = 300°C  
 P = 2000 psig  
 Time = 60 min.

Coal = Wyodak or Illinois #6  
 Catalyst = Zinc Chloride  
 Solvent = 70 ml

Run No.	Coal Type	Solvent Type	Catalyst, g	Sol., % maf	Extract H/C	Analysis N/C	<sup>1</sup> H-NMR H <sub>al</sub> /H <sub>ar</sub>	Data f <sub>a</sub>
69	Wyodak	Cyclohex	0.0	6.9	1.44	0.0053	>10.	-
25	Wyodak	Cyclohex	5.0	13.5	1.33	0.0015	7.5	0.41
35	Wyodak	Benzene	0.0	7.4	1.58	0.0114	10	-
36	Wyodak	Benzene	5.0	26.2	1.22	0.0059	4.4	0.50
29	Illin. #6	Cyclohex.	0.0	1.8	-	-	-	-
42	Illin. #6	Cyclohex.	5.0	8.0	1.09	0.0018	3.3	0.58
37	Illin. #6	Benzene	0.0	3.5	1.15	0.0124	4.7	0.52
38	Illin. #6	Benzene	5.0	11.0	1.03	0.0027	3.0	0.61

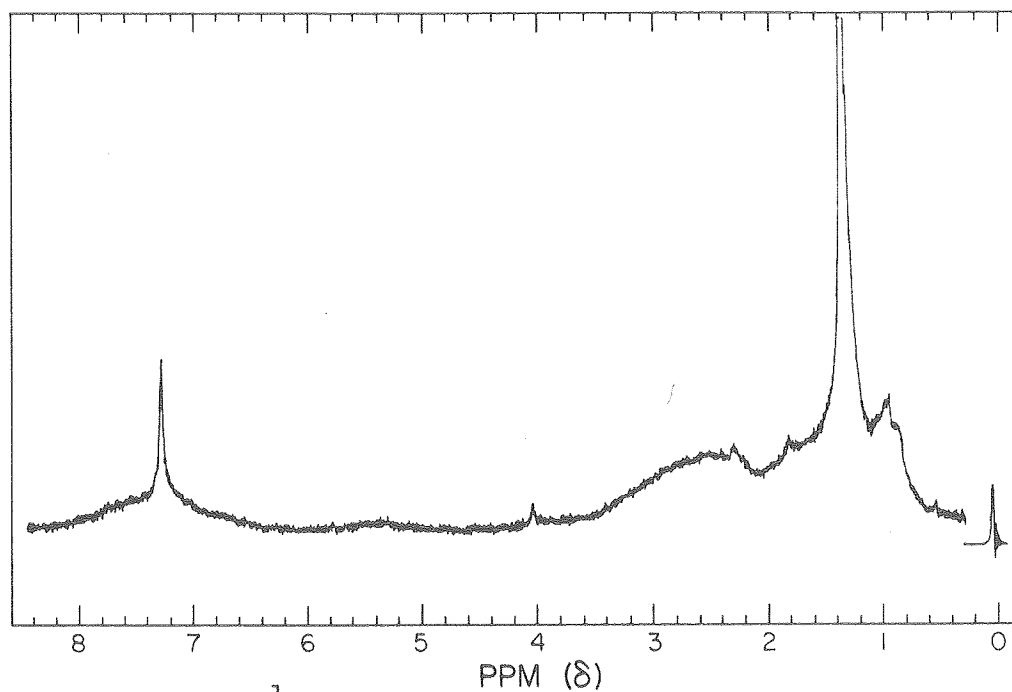
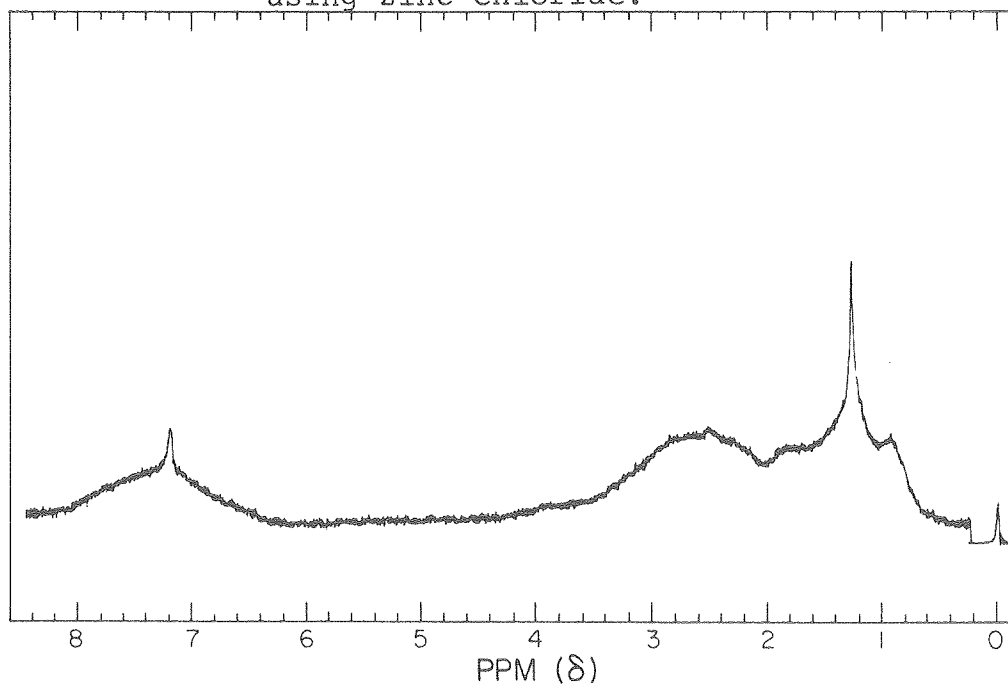


Figure 3-15.  $^1\text{H}$ -NMR Spectrum of Extract obtained from Wyodak, reacted in Benzene at 300°C and 2000 psig, using Zinc Chloride.



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Figure 3-16.  $^1\text{H}$ -NMR Spectrum of Extract obtained from Illinois #6 Coal, reacted in Benzene at 300°C and 2000 psig, using Zinc Chloride Catalyst.

#### D. General Observations

##### 1. Analysis of the Coal Residues

Most of the characterization performed during the course of this study was conducted on the soluble material, i.e. the extract. However, some effort was also devoted to study the effect of the reaction on the residue, which represented that portion of the coal substrate not soluble in the solvent. The information obtained during this phase of the investigation consisted of the percent residue soluble in pyridine and the H/C ratio of the various residue fractions. The residues were first washed with distilled water at 90°C, in order to remove as much of the zinc chloride as possible. The washed residue was then extracted with pyridine using standard Soxhlet extraction procedures. This characterization was performed on selective runs, and the results of the work are summarized in Table 3-17.

Several observations are made in studying the extraction data. First, the presence of zinc chloride resulted in a total pyridine solubility increase from 17.4% to 69.2% at 300°C, 2000 psig, and catalyst to coal weight ratio of 0.5. This definitely indicates that the zinc chloride was acting as a positive catalyst. Secondly, the extraction data shown that increasing the catalyst to coal weight ratio from 0. to 0.5 causes the pyridine solubility to rise; however, any further increase in the catalyst loading causes the pyridine solubility to drop. This shows that zinc chloride

TABLE 3-17

## Pyridine Solubility Data on Coal Residues after Reaction

Run No.	Coal Type	Cat./Coal Weight Ratio	Temp. <sup>a</sup> °C	Cyclohexane <sup>b</sup> Solubility, % maf	Pyridine <sup>c</sup> Solubility % maf	Total Solubility, % maf
69	Wyodak	0.0	300	6.9	10.5	17.4
54	Wyodak	0.5	300	19.3	49.9	69.2
25	Wyodak	1.0	300	13.5	31.0	44.5
47A	Wyodak	1.0	300	13.5	32.3	45.8
47B					29.1	42.6
47C					29.0	42.5
68	Wyodak	1.0	400	28.4	18.9	47.3
42	Illin. #6	1.0	300	8.0	39.4	47.4

<sup>a</sup>All reactions were carried out at 2000 psig of H<sub>2</sub> measured at reaction temperature.

<sup>b</sup>In-situ cyclohexane solubility.

<sup>c</sup>Soxhlet extraction with pyridine.

in excess amounts could be leading to retrograde reactions and resulting in polymerization. This trend was also noted for the cyclohexane solubility data presented in section "A" of this chapter.

Comparing the effect of the reaction on Wyodak versus Illinois #6 coal shows that the pyridine solubility for the Illinois #6 coal is higher than that for the Wyodak coal. This is in contrast to the cyclohexane data. Thus the reaction resulted in greater increase of oils for the Wyodak coal, but a greater increase of preasphaltenes for the Illinois #6 coal.

Another observation is that an increase in the reaction temperature (Run #68) resulted in a higher yield of cyclohexane soluble products; however, the pyridine solubility decreased. A possible reason for this could be that enhanced cracking occurring at the higher temperatures causes a greater transfer of hydrogen from the residue to terminate the fragments formed. Such a process might induce the formation of a more aromatic residue containing a larger number of fused ring segments and thereby reduce the pyridine solubility of the residue.

Finally, Runs 47A, B, and C are presented in Table 3-17 to show that adequate reproducibility of the pyridine solubility data was attained. Three residue fractions from the same reaction (Run #47) were Soxhlet extracted separately. The resulting extraction data were within 3.3% of each other.

In addition to conducting pyridine extractions, elemental analyses were also obtained for the various residue fractions. As illustrated in Table 3-18, the data indicate that the H/C ratios of the cyclohexane soluble fractions are consistently higher than that of the non-cyclohexane soluble fraction and that of the starting coal. Table 3-18 also shows that the pyridine extractable fractions of the residues have higher H/C ratios than the non-pyridine soluble fractions.

## 2. $H_{al}/H_{ar}$ Ratio and Aromaticity versus H/C Ratio

The  $H_{al}/H_{ar}$  ratio and aromaticity,  $f_a$ , obtained for each extract, were plotted versus the H/C ratio. The resulting plots, presented in Figures 3-17 and 3-18, indicate that the  $H_{al}/H_{ar}$  ratio increases with the H/C ratio, while the  $f_a$  decreases with increasing H/C ratio. This is consistent with the expectation that the extract becomes less aromatic as the H/C ratio increases. Figure 3-17 also shows that the  $H_{al}/H_{ar}$  ratio increases more rapidly than the H/C ratio. It should be noted that the scatter in the  $H_{al}/H_{ar}$  data reflects the difficulty in obtaining precise ratios, since the  $H_{ar}$  counts were quite small compared to the  $H_{al}$  counts.

Finally, both the plots show that lower  $H_{al}/H_{ar}$  ratios and higher  $f_a$  were obtained using the Illinois #6 coal than the Wyodak coal. Since Illinois #6 coal has a higher aromatic carbon content than the Wyodak coal, the trend

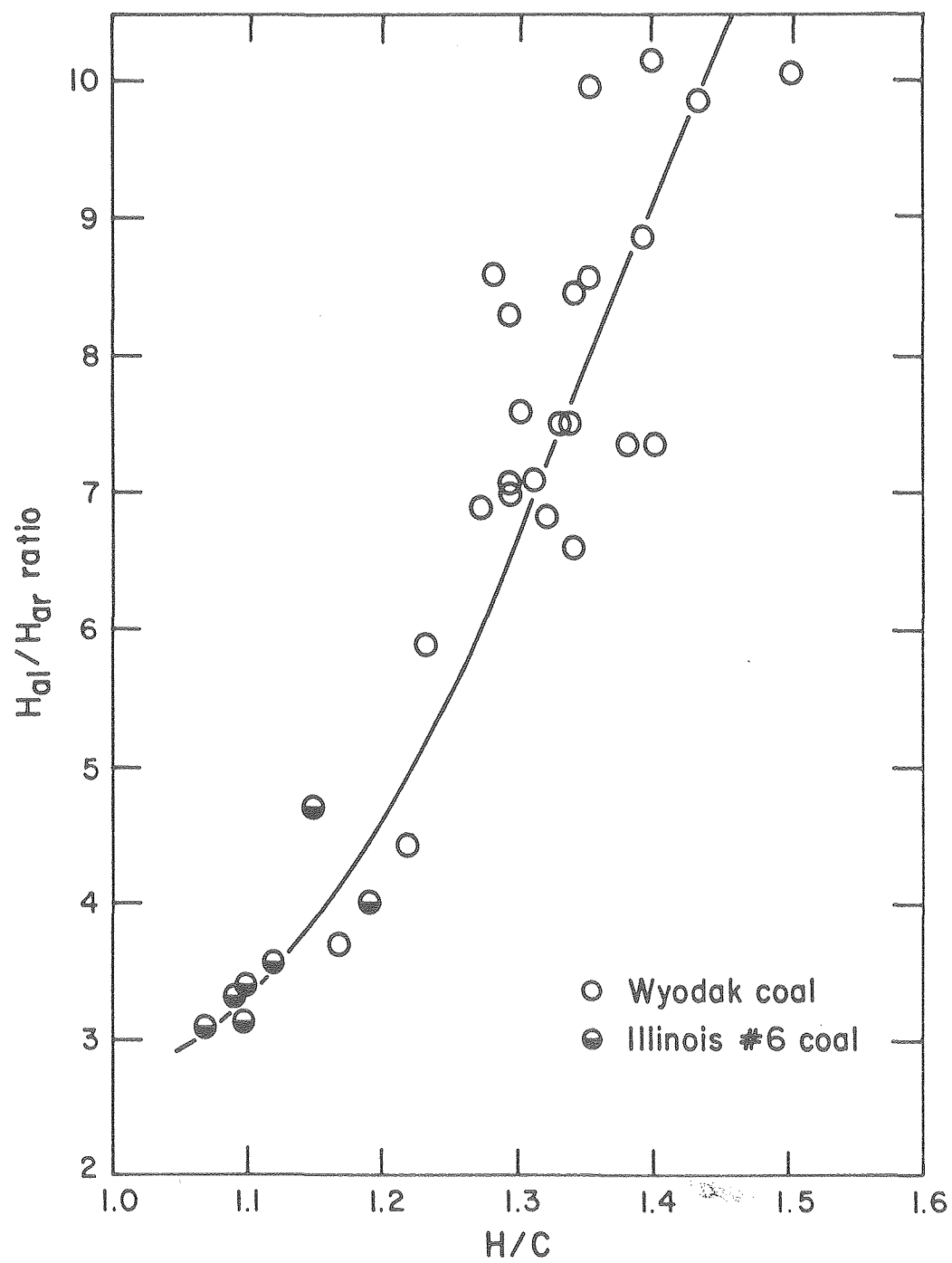
TABLE 3-18

Effect of Reaction on H/C Ratios of Different Extractable Fractions

Run No.	Coal Type	Cat./Coal Weight Ratio	Temp. <sup>a</sup> °C	H/C Raw Coal	H/C Ratio Cyclohex. Soluble Fraction	H/C Ratio Non-Cyclohex. Soluble Fraction	H/C Ratio Pyridine Soluble Fraction	H/C Ratio Non-Pyrid. Soluble Fraction
69	Wyodak	0.0	300	0.98	1.44	0.91	1.25	0.87
54	Wyodak	0.5	300	0.98	1.28	1.05	1.07	0.98
25	Wyodak	1.0	300	0.98	1.33	0.85	0.98	0.75
47A	Wyodak	1.0	300	0.98	1.38	0.90	0.95	-
47B						0.86	0.98	0.73
47C						0.82	1.01	0.74
68	Wyodak	1.0	400	0.98	1.17	0.71	1.12	0.64
42	Illin. #6	1.0	300	0.83	1.09	0.90	0.95	0.81

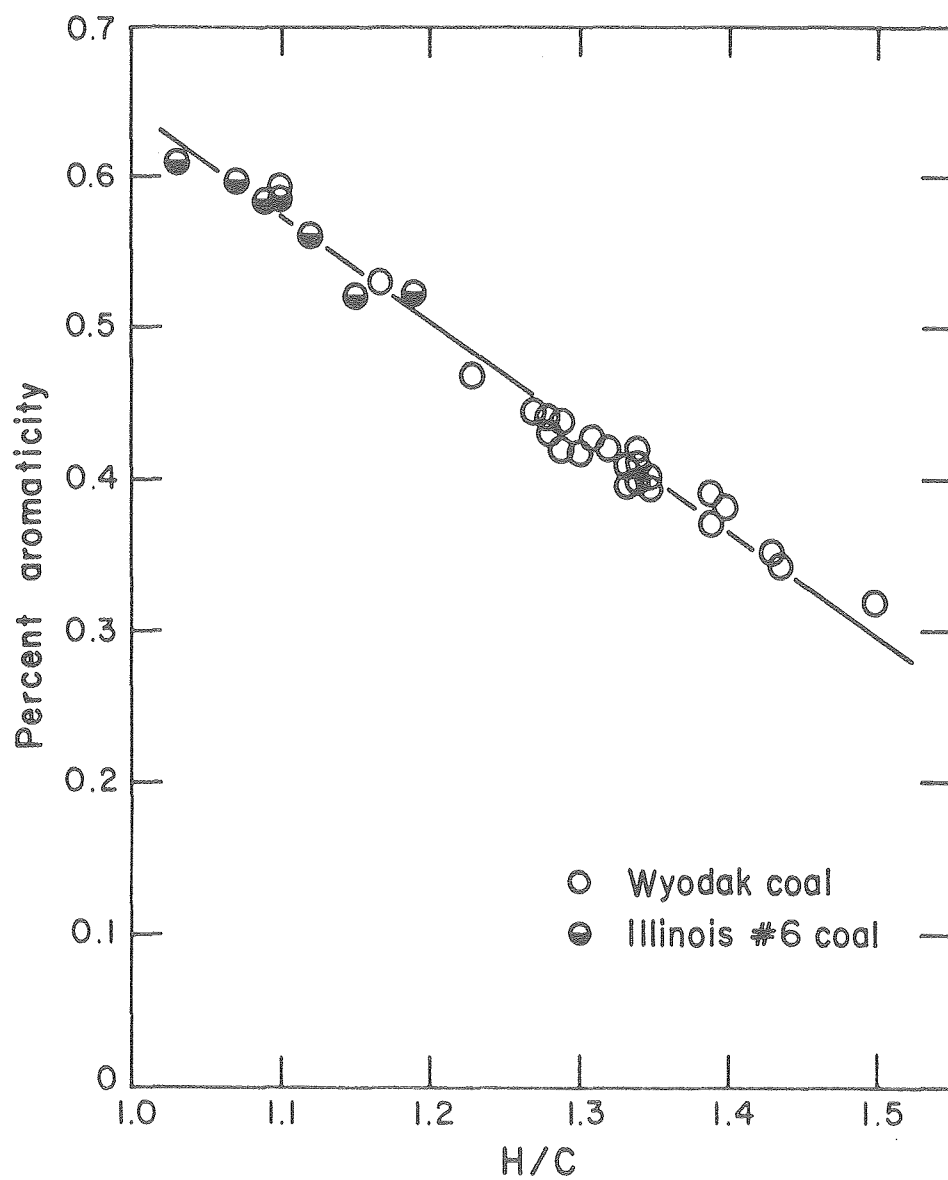
<sup>a</sup>All reactions were carried out at 2000 psig of H<sub>2</sub> measured at reaction temperature.





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Figure 3-17. H/C vs.  $H_{al}/H_{ar}$  Plot for all Coal Extracts



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Figure 3-18. H/C vs. Percent Aromaticity for all Coal Extracts.

was expected, indicating that the more aromatic coal resulted in oil like products which were also more aromatic. However, the data for both coals lie along the same line regardless of the initial aromatic content. In addition, data for SRC-I extracts, reported by Tanner and Bell (18), also lie along the same line when it is extrapolated to the more aromatic region of the plot.

#### IV. CONCLUSIONS

This investigation has provided data on the use of zinc chloride as a coal liquefaction catalyst in an extracting solvent medium. On the basis of the experimental results obtained, the following conclusions can be presented:

1. The use of zinc chloride results in increased cyclohexane solubility for SRC-I, Wyodak coal, and Illinois #6 coal, the principal substrates investigated in this study. For example, at the base experimental conditions of 300°C, 2000 psig 60 minutes reaction time, and a catalyst to coal weight ratio of 1.0, the cyclohexane solubilities of SRC-I, Wyodak coal, and Illinois #6 coal are 30.0%, 13.6%, and 8.0%, respectively. In contrast, the cyclohexane solubilities of SRC-I, Wyodak coal, and Illinois #6 coal reacted under similar conditions but without the presence of zinc chloride are 10.6%, 6.9%, and 1.8%, respectively.

2. Data on the effect of catalyst loading for Wyodak coal at 300°C, 2000 psig and 60 minutes reaction time, show that a maximum solubility of 20.0% was achieved at a catalyst to coal weight ratio of 0.6. Data for Illinois #6 coal at similar reaction conditions show that a maximum solubility of 8.0% occurred at a catalyst to coal weight ratio of about 1.0.

3. Data on increasing reaction time at constant temperature and pressure of 300°C and 2000 psig and catalyst to coal weight ratio of 1.0 show that the solubility of

Wyodak coal increases up to 120 minutes, after which the solubility is approximately constant. In contrast, a similar set of experimental runs with SRC-I show that the extraction of the solvent refined coal is nearly complete after about 60 minutes.

4. Data on increasing reaction temperature at constant pressure of 2000 psig, 60 minute reaction time, and catalyst to coal weight ratio of 1.0 indicate that the solubility of Wyodak coal, both with and without zinc chloride, increases linearly between 250°C and 400°C. However, the solubility of the coal in the presence of zinc chloride is approximately double that observed in the absence of catalyst at the same reaction temperature.

5. The effects of increasing hydrogen pressure on the solubility and characteristics of the double products are not as great as those of temperature. However, the solubility of Wyodak in cyclohexane does increase from 10.6% to 17.3% as the hydrogen pressure is increased from 680 psig to 3000 psig at constant temperature of 300°C, 60 minutes reaction time, and catalyst to coal ratio of 1.

6. For Wyodak coal and Illinois #6 coal, the  $H_{al}/H_{ar}$  and H/C ratios of the extract decrease as the cyclohexane solubility increases. This trend was observed for both coals regardless of the manner in which the higher cyclohexane solubility was obtained. In contrast, a different trend was observed with SRC-I, in which case the  $H_{al}/H_{ar}$

ratio of the extract increases with increasing cyclohexane solubility.

7. Experiments with co-catalysts indicated that a nickel-zinc chloride mixture results in increased cyclohexane solubility for Illinois #6 coal. The cyclohexane solubility of Illinois #6 coal increased from 8.0% with zinc chloride alone to 12.6% with a nickel- zinc chloride mixture. Studies with other co-catalysts indicated that zinc- zinc chloride mixtures and NiS- zinc chloride mixture are ineffective in increasing the cyclohexane solubility. Finally, aluminum chloride- zinc chloride mixtures produced lower SRC-I solubilities than could be achieved using zinc chloride alone, indicating that aluminum chloride has a detrimental effect on the solubilization of coal.

8. The cyclohexane solubility of the three coals used in this study increased significantly when either methanol, ethanol, or isopropanol was used in conjunction with zinc chloride. This is most probably due to extensive alkylation of the coal. In contrast, t-butanol under similar conditions produced lower solubilities.

9. Two impregnation methods were studied in order to improve catalyst- coal contacting. Both studies revealed that impregnation of the catalyst into the coal using methanol solution before conducting the reaction does not increase the cyclohexane solubility over that which is achieved without impregnation.

10. Experimental work with Wyodak coal using varying amounts of solvent revealed that a change in solvent to coal ratio from 7 ml/g to 21 ml/g produces no change in the cyclohexane solubility.

11. Several experiments were conducted in benzene solvent instead of cyclohexane solvent. The data for both Wyodak coal and Illinois #6 coal indicate that the solubilities in benzene are higher, and the resulting extracts have lower H/C and  $H_{al}/H_{ar}$  ratios than the extracts obtained from cyclohexane solubilization.

12. Soxhlet extraction with pyridine of that portion of the coal not solubilized in cyclohexane indicated that zinc chloride also increases the asphaltene and pre-asphaltene content of the reacted coal. Total pyridine solubilities of up to 69.2% were obtained for reaction of Wyodak coal at 300°C, 2000 psig, and a catalyst to coal weight ratio of 0.5. In contrast, a total pyridine solubility of only 17.4% was obtained without the use of zinc chloride under identical reaction conditions.

13. The cyclohexane soluble extracts in all cases have substantially higher H/C ratios than the parent coal. In addition, extracts from Wyodak coal have higher H/C ratios and are more aliphatic than the extracts from Illinois #6 coal.

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